THE

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OF THE

ROYAL DUBLIN SOCIETY.

VOLUME IX.—(SERIES II.)

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CONTENTS.

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I.

ON SECONDARY RADIATION (PART II.), AND ATOMIC STRUCTURE.

BY

J. A. McCLELLAND, M.A.,

Professor of Experimental Physics, University College, Dublin.

Price One Shilling.

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ON SECONDARY RADIATION (PART II.), AND ATOMIC STRUCTURE.

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This paper is a continuation of one on Secondary Radiation recently published.[*]

In that paper it was shown that when the β and γ rays of radium are allowed to penetrate a substance, it emits a secondary radiation of negatively-charged particles. The penetrating power of this secondary radiation was measured, and its deflexion in a magnetic field was compared with that of the primary β rays, and the result showed that the primary and secondary β rays were similar in character.

The relative intensity of this secondary β radiation given by a few different substances was compared; and, in the case of elementary substances, the atomic weight appeared to be the chief factor in determining the intensity. This point has been fully tested in the present paper, the secondary radiation from a large number of elements being measured under similar conditions, and the result indicated in the previous paper has been fully confirmed, the secondary radiation being always greater, the greater the atomic weight of the radiating substance.

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[*] Trans. Roy. Dublin Soc., Vol. VIII., Part XIV., 1905, p. 169, and Phil. Mag., Vol. IX. (Ser. VI.), 1905, p. 230.

Apparatus and Method of Observation.

The apparatus described in the previous paper is here somewhat modified to enable measurements to be made with substances in the form of powders or as liquids.

The radium is placed at R, so that a stream of β and γ rays passes through a hole in a thick lead screen, and falls on a plate P of the substance under examination, which is supported on a stand S. When a liquid or powder is used, it is contained in a small tray with very thin mica walls, so that little radiation comes from the walls of the containing vessel.

The secondary radiation is measured by the ionisation it produces in the vessel T; this is a brass tube of 20 cms. length, and 7·5 cms. internal diameter, the end towards P being covered with a sheet of tinfoil about ·013 mm. thick. An inner terminal, insulated by a paraffin cork, is fixed along the axis of T, and joined to a Dolezalek electrometer; T is kept at a high potential by joining it to storage cells, and the rate of charge of the inner terminal is measured by the electrometer in the usual way.

The distance from R to P is about 25 cms., and from P to the tube T about 9·5 cms. The secondary radiation has therefore to pass through 9·5 cms. of air, and a sheet of tinfoil ·013 mm. thick, before it reaches the ionisation chamber; any easily-absorbed radiation is therefore excluded, and, as shown in the previous paper, we are dealing with a radiation consisting only of β particles.

The vessel containing the radium and the air-space between it and the plate P absorbs all the α rays and the more easily-absorbed β rays, so that the radiation acting on the plate P is of a penetrating character, consisting, as it does, of the more penetrating β rays and of γ rays.

A large number of elements have been compared by this apparatus as regards the intensity of the secondary radiation from them. Some of the substances were in the form of plates 5 cms. square; others were used as powders. In that case they were contained in small mica trays of the same size, and, to make the conditions as much alike as possible, substances which were only available as powders were tested against another substance in powder which was also available in the form of a plate.

In every case a sufficient thickness was used to absorb all the incident β rays. Too small a value was assigned to aluminium in the previous paper, because a sufficient thickness was not used: the scale of the other numbers in that paper is also somewhat altered by making a small correction in the value of the secondary radiation from lead. Great care has been taken in comparing substances which give nearly the same secondary radiation, so as to place them in the proper order; and it is believed that the errors of observation will not be found to have in any

case reversed the proper order. Possibly the substances of very small density may have too small a value assigned to them, as in their case a thick plate or layer was necessary, which could not, therefore, be in quite the same position relative to the ionisation-tube *T.* In every case the upper surface of the substance was
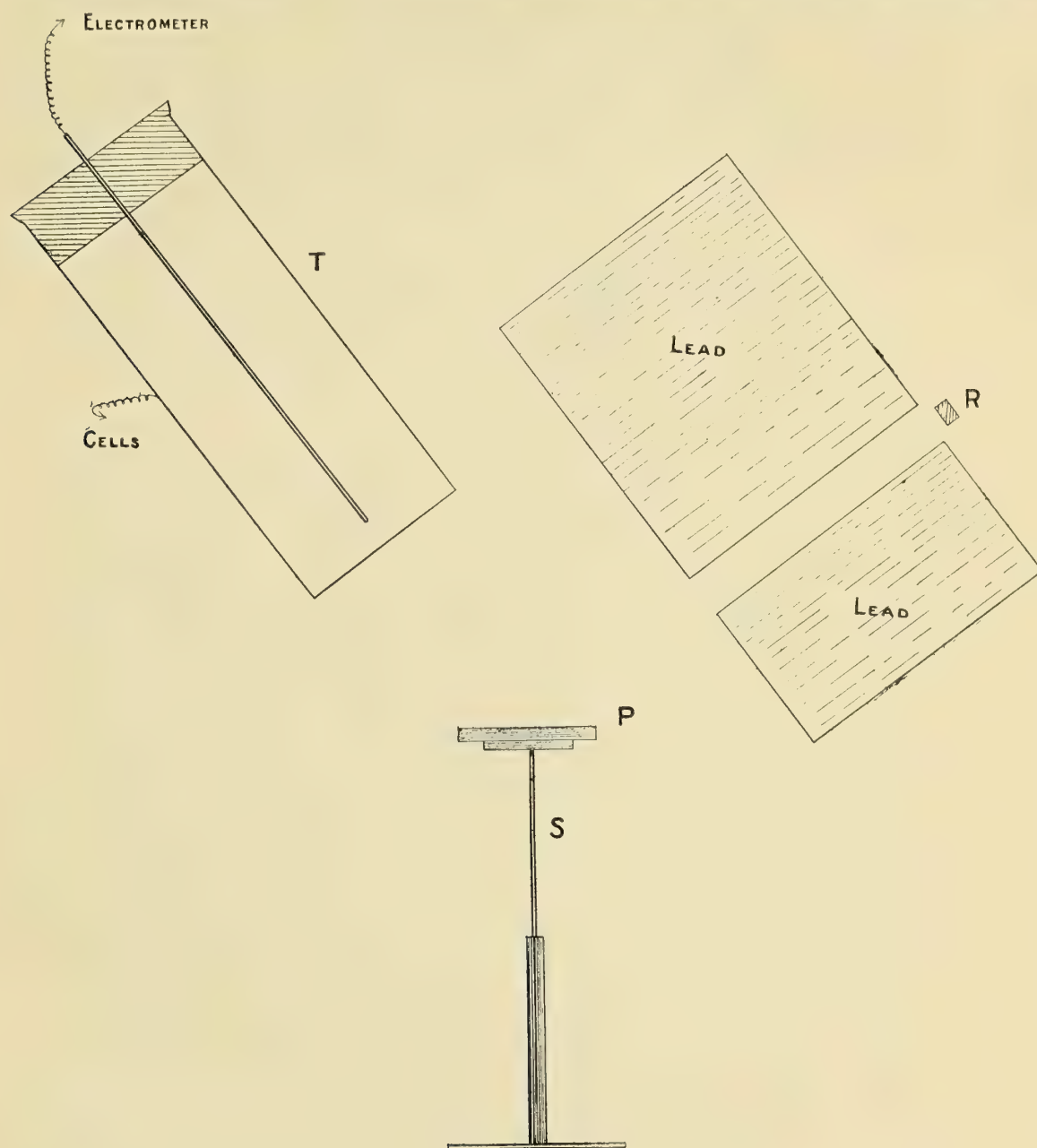

Fig. 1.

placed in exactly the same position. Of course corrections were always applied for whatever small ionisation existed when the plate *P* was removed, and the stand *S* lowered.

It should be here pointed out that the intensity of the secondary radiation is measured by the ionisation it produces in the vessel *T*, and, if the radiations from different substances are not exactly similar in character, this method may be open to some objection—for example, if the secondary rays from one substance are more easily absorbed than those from another.   The secondary radiation from lead was studied in detail as described in the previous paper, and it was found to be very similar to the primary β rays; but the secondary radiation from the other substances has not been studied in detail.   In any case the remarkable dependence of the secondary radiation thus measured on the atomic weight of the substance holds true.

Secondary Radiation from Different Substances.

The following Table shows the results of the investigation :—

Table.

Substances.	Secondary Radiation.	Atomic Weight.	Ratio of Secondary Radiation to Atomic Weight.	Density.
Uranium, . . .	100	239·5	·41	18·7
Bismuth, . . .	97	208·5	·46	9·8
Lead, . . .	97	206·9	·46	11·4
Mercury, . . .	96	200·3	·47	13·6
Platinum, . . .	93	194·8	·47	21·5
Tungsten, . . .	88	184·0	·47	19·1
Iodine, . . .	85·5	127·0	·67	5·0
Antimony, . . .	85	120·0	·71	6·7
Tin, . . .	84	118·5	·71	7·3
Cadmium, . . .	82	112·4	·73	8·6
Silver, . . .	81	107·9	·75	10·5
Molybdenum, . .	78	96·0	·81	8·6
Selenium, . . .	74	79·1	·94	4·3
Arsenic, . . .	73	75·0	·97	5·7
Zinc, . . .	72	65·4	1·10	7·2
Copper, . . .	71	63·6	1·11	8·9
Cobalt, . . .	67	59·0	1·13	8·9
Nickel, . . .	67	58·7	1·14	8·5
Iron, . . .	65	55·9	1·16	7·7
Chromium, . . .	63	52·1	1·20	6·5

Table—*continued.*

Substances.	Secondary Radiation.	Atomic Weight.	Ratio of Secondary Radiation to Atomic Weight.	Density.
Calcium,	55	40·1	1·37	1·6
Potassium,	54	39·1	1·38	0·9
Sulphur,	53·5	32·06	1·67	2·07
Phosphorus,	53	31·0	1·71	1·8
Aluminium,	48	27·1	1·77	2·7
Magnesium,	43	24·4	1·76	1·7
Sodium,	42	23·0	1·82	0·97
Carbon,	35	12·0	2·91	1·8

DISCUSSION OF RESULTS.

Throughout the table the secondary radiation is greater, the greater the atomic weight. It was not found possible to distinguish between bismuth and lead, although there is a small difference of atomic weight.

The secondary radiation is not proportional to the atomic weight. As the atomic weight increases, the secondary radiation increases, but less rapidly. The ratio of secondary radiation to atomic weight is given in the fourth column of the table.

The elements given in the above table fall into well-defined divisions in a striking manner if we plot a curve as in fig. 2 with atomic weight as abscissa and secondary radiation as ordinate. Carbon is in one division, and is the only member of that division given in the table; sodium, magnesium, aluminium, phosphorus, and sulphur form a second division; potassium, calcium, chromium, iron, nickel, cobalt, copper, zinc, arsenic, and selenium form a third division; molybdenum, silver, cadmium, tin, antimony, and iodine a fourth; tungsten, platinum, mercury, lead, and bismuth a fifth; and uranium is in a sixth division.

It will be observed that this method of division corresponds exactly to the division of the elements into "periods" employed in chemistry. The divisions mentioned above correspond in order to the first and second short periods, the first, second, fourth, and fifth long periods. Our table contains no member of the third long period, the space for it occurring between iodine and tungsten.

The elements contained in each chemical period lie on a part of the curve which is practically a straight line. Going from one period to the next there is very little increase of secondary radiation, so that there is a marked change in

the slope of the curve at these parts. The flattening begins at or near the top of each period, and when we get into the next period, a more rapid increase of secondary radiation again sets in.

Several of the periods are very incomplete—for example, a number of elements are missing below molybdenum; and, as stated above, we have no representative of the third long period; but still enough of the whole curve is drawn to show that there is a decided change of form going from one period to the next as compared with the form throughout any period.

The flattening of the curve going from one period to another is a flattening of the top of the curve corresponding to one period rather than that of the lower portion of the curve corresponding to the next period.

Again, although we have only one element in the first and last periods—carbon and uranium—still it is obvious that they give points on what are distinct portions of the curve, as in the case of the other periods.

We shall now see how these results may possibly be explained. The prominent fact is that the secondary radiation increases as the atomic weight increases, and it is easy to picture in a general way how this result may be brought about. The incident primary radiation consists chiefly of β particles, each of which is small compared with an atom as a whole, so that we must regard each primary β particle as colliding with or coming within the radius of action of an electron (or β particle) of the atom of the substance being tested for secondary radiation rather than with the atom as a whole. If, then, all atoms are composed of electrons, we shall have for a given incident primary radiation the same number of electrons disturbed in the substance tested, no matter what substance it is. The greater the atomic weight of the substance, the greater, therefore, is the disturbance produced in any one atom, and the greater the chance of detaching electrons to produce our secondary radiation.

Then, in addition to the general result that the secondary radiation increases with the atomic weight, we have the division of the elements as shown in the table of results, and especially by the curves in fig. 2.

We might describe the results shown by these curves by saying that as we pass through the members of a chemical period, the secondary radiation increases fairly rapidly as the atomic weight increases; but as we go from one period to the next, the increase of secondary radiation with atomic weight is much less rapid. When we get near the top of a period, there is very little increase of secondary radiation as the atomic weight increases; but when we get into the next period, the secondary radiation again begins to increase more rapidly. The curve, if completed by the inclusion of the missing elements, would apparently have a flattened portion corresponding to the top of each period. Following the same line of explanation as before, this can be explained as follows:—Going from
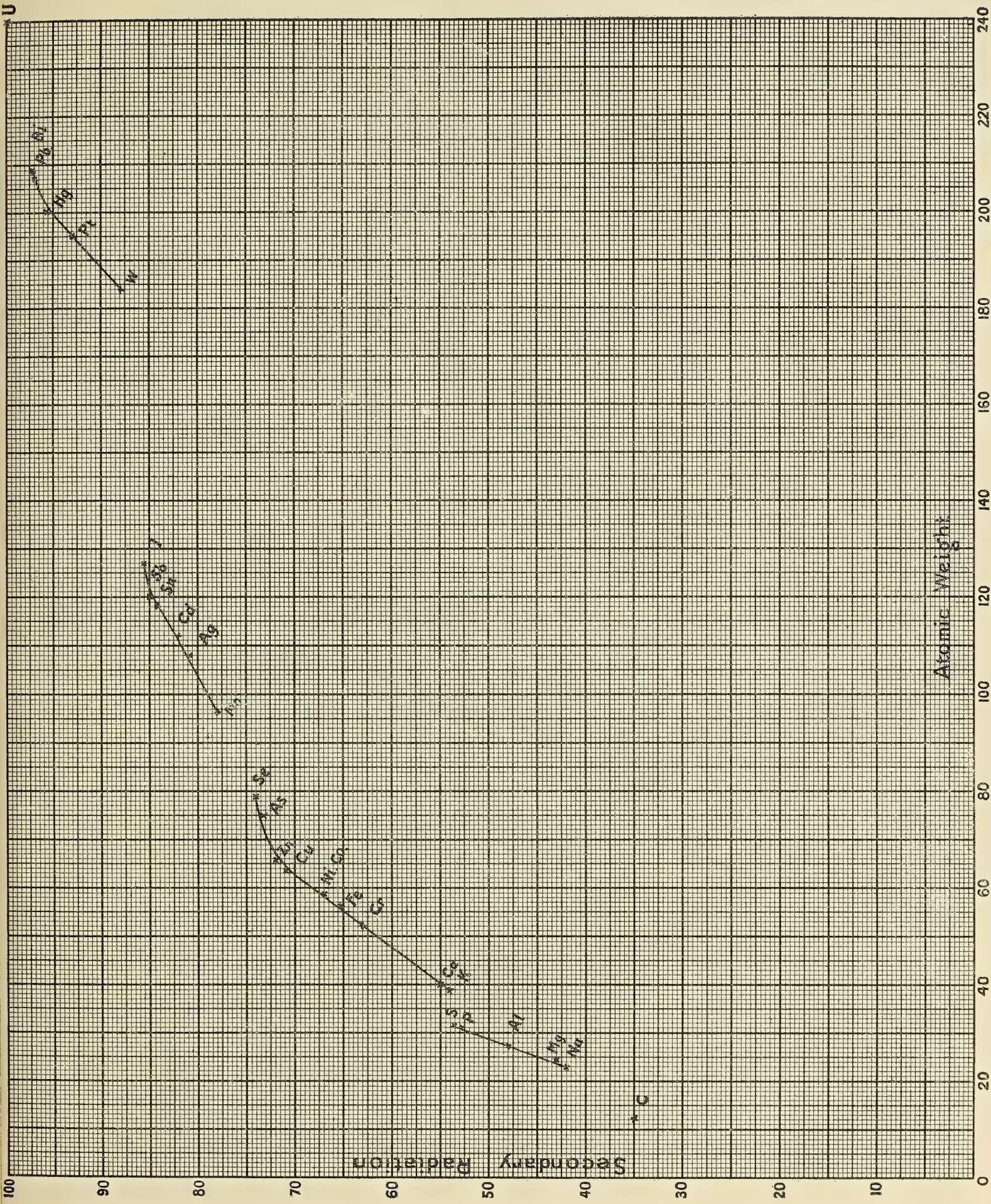
Fig. 9.

one element to another of greater atomic weight in the same period, the additional electrons necessary to form the heavier atom are added on in a way that increases considerably the secondary radiation; but in passing from one period to the next, the additional electrons are added on in some different way which is not so effective in producing an increase of secondary radiation.

Again, we know that members of the same period have little in common chemically, but that each member of any period corresponds chemically to some members of the other periods. The electrons, therefore, which are added on as we go through a period, are those which determine the chemical properties, and are also those which are chiefly effective in increasing the secondary radiation.

Let us further see how the chemical "groups" are represented on our curves; each chemical group is composed of elements having similar chemical properties. If we divide the curves corresponding to the long periods into two parts (as these periods are divided by the chemist into odd and even "series") at the places where the *transitional* elements occur, that is about iron, cobalt, and nickel in one case, slightly below silver in the second case, and at platinum in the third case, and regard each part as a separate curve, then we can say that each chemical group is made up of elements occupying similar positions on our curves, when completed so as to contain all the elements. The curves corresponding to short periods are, of course, to be taken as a whole.

Both the periods and the groups in the periodic divisions of the elements employed in chemistry are therefore represented in our curves in a very simple manner.

Our results have therefore led to the view that the manner in which additional electrons are added on to form elements of greater atomic weight is different as we go from one period to the next, from what it is as we pass through elements not near the ends of a period. It will at once be seen that there is a close resemblance in this to the views advanced during recent years by J. J. Thomson as to the constitution of the atom ("Electricity and Matter," and various papers). Professor Thomson deduces, from theoretical investigations on stability, that, as the number of electrons in the atoms are increased, they may take up a position on an outer shell, or they may go to form a central core, thus giving in general two different ways of adding on the additional electrons.

In conclusion, there are a few points in connexion with the numbers in the Table which may be noticed.

The density of the substances is given in the fifth column, and we see that the density is of little importance in determining the secondary radiation. It might appear at first sight that the coefficient of absorption, which is approximately proportional to the density, should be an important factor, because it determines

for the primary rays the depth of the substance penetrated, and the coefficient of absorption of the secondary rays determines the depth from which they can come. It is easy to show, however, that the secondary radiation given off by a plate, arranged as in fig. 1, is proportional to

$$\frac{\lambda}{\lambda + \lambda'},$$

where λ is the coefficient of absorption of the primary rays, and λ' that of the secondary rays. If, then, $\lambda = \lambda'$, the secondary radiation will not depend on the coefficient of absorption of the substance used. Experiments described in the previous paper showed that in the case of lead, at any rate, this relation was approximately fulfilled.

Another point to be noticed is that the secondary radiation from uranium is not abnormal in any way; the secondary radiation is what was to be expected from an element of its atomic weight, and the fact that it is a radio-active substance has produced no abnormal effect. It must be remembered, however, that the first stage in radio-activity consists in the emission of α particles, while the radiation we are dealing with is one of β particles only. The breaking up of the atom of a radio-active substance may arise, not from the instability of electrons, but from the instability of positive parts.

It may also be mentioned that phosphorus was tested both in the amorphous form and as yellow phosphorus, but no difference in radiating power was detected.

I have pleasure in thanking Dr. Adeney, who supplied me with most of the elements used, and also Mr. J. H. Pollok, to whom I am greatly indebted for the trouble he took in preparing some metallic uranium.

TRANSACTIONS (SERIES II.).

VOLUME IX.

Part

1. On Secondary Radiation (Part II.), and Atomic Structure. By J. A. McClelland, M.A., Professor of Experimental Physics, University College, Dublin. (May 17, 1905.) 1s.

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THE ENERGY OF SECONDARY RADIATION.

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By J. A. M'CLELLAND, M.A., Professor of Experimental Physics, University College, Dublin.

In previous papers* the author has studied the secondary radiation emitted by substances when exposed to the action of the β and γ rays from radium. This secondary radiation consists of negatively-charged particles similar to the β rays; and a simple relation has been found to exist between the intensity of the radiation and the atomic weight of the substance emitting it, the secondary radiation from all the elements tested increasing with the atomic weight of the element.

In establishing this relation, the relative intensities of the secondary radiations from a large number of elementary substances were compared, the incident radiation of β rays being the same in all cases; but no attempt was made to compare the energy of the secondary radiation with that of the primary radiation producing it. The present paper deals with this main point, together with a number of other points that arise in connexion with it.

PRELIMINARY INVESTIGATION.

The apparatus used in the previous work was of such a form as to exclude any easily-absorbed secondary radiation that might be produced when the incident β (and γ) rays were absorbed by any substance; the secondary radiation experimented with consisted entirely of negatively-charged particles similar in penetrating power to the primary β rays. As our present object is to establish the relation between the total energy of the secondary radiation and that of the primary radiation producing it, it is necessary to determine,

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* Trans. Royal Dublin Soc., Vol. viii., Part xiv., 1905, p. 169, and Vol. ix., Part i., 1905, p. 1.

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in the first place, whether or not any easily-absorbed radiation is produced at the surface of a substance which is exposed to β rays.

This was investigated in the following manner :—

Two thick lead plates were insulated and placed parallel to each other, the upper having a hole at the centre, covered only with tinfoil, through which passed a stream of β rays from the radium. The whole was enclosed in an air-tight vessel which could be exhausted to any desired pressure. One plate was kept at a high potential by joining it to a battery of small cells; the other plate was connected to an electrometer, and the saturation-current between the plates was measured in the usual way.

In some experiments the plate connected to the electrometer was provided with a guard-ring.

The pressure was reduced step by step; and the saturation-current was measured at each step.

Now the total ionisation between the plates is due to two possible causes: first, the penetrating rays direct from the radium, together with the penetrating secondary radiation emitted by the plates—meaning by penetrating radiation one that can readily pass through the space between the plates without suffering any marked diminution of intensity even at atmospheric pressure; secondly, there may be an easily-absorbed radiation produced at the surface of the plates which will be completely stopped in the first few millimetres of air when at atmospheric pressure.

When the pressure is reduced, the ionisation due to the first cause will obviously be proportionately reduced; but the ionisation due to the second cause will not be diminished, as this radiation will merely penetrate a greater thickness of the rarefied air, and produce the same ionisation as before, until the pressure is so much reduced that the easily-absorbed radiation reaches the opposite plate before being completely stopped. If, therefore, we plot the saturation-current against the pressure, the curve should be a straight line if there is no easily-absorbed radiation present; if there is such a radiation, the curve should be a straight line at low pressures, but becoming less inclined to the axis of pressure at higher pressures. The change of slope will obviously occur at different pressures for different distances between the plates.

A number of experiments were made in this way with the plates at different distances apart in different experiments varying from 2 mm. to 130 mm., the pressures being varied in each experiment from atmospheric down to a few centimetres of mercury. In every case the saturation-current was strictly proportional to the pressure throughout the whole range of pressures, the curve of current against pressure being a straight line passing through the origin.

To test how the method worked, the radium was removed, and a little uranium oxide placed on the lower plate. We know that the radiation passing between the plate in this case does contain easily-absorbed α rays. It was found that with the plates less than 10 mm. apart, the current was approximately proportional to the pressure up to atmospheric pressure; but at greater distances apart, the curve of current against pressure was at first a line through the origin becoming nearly parallel to the axis of pressure as the pressure was increased.
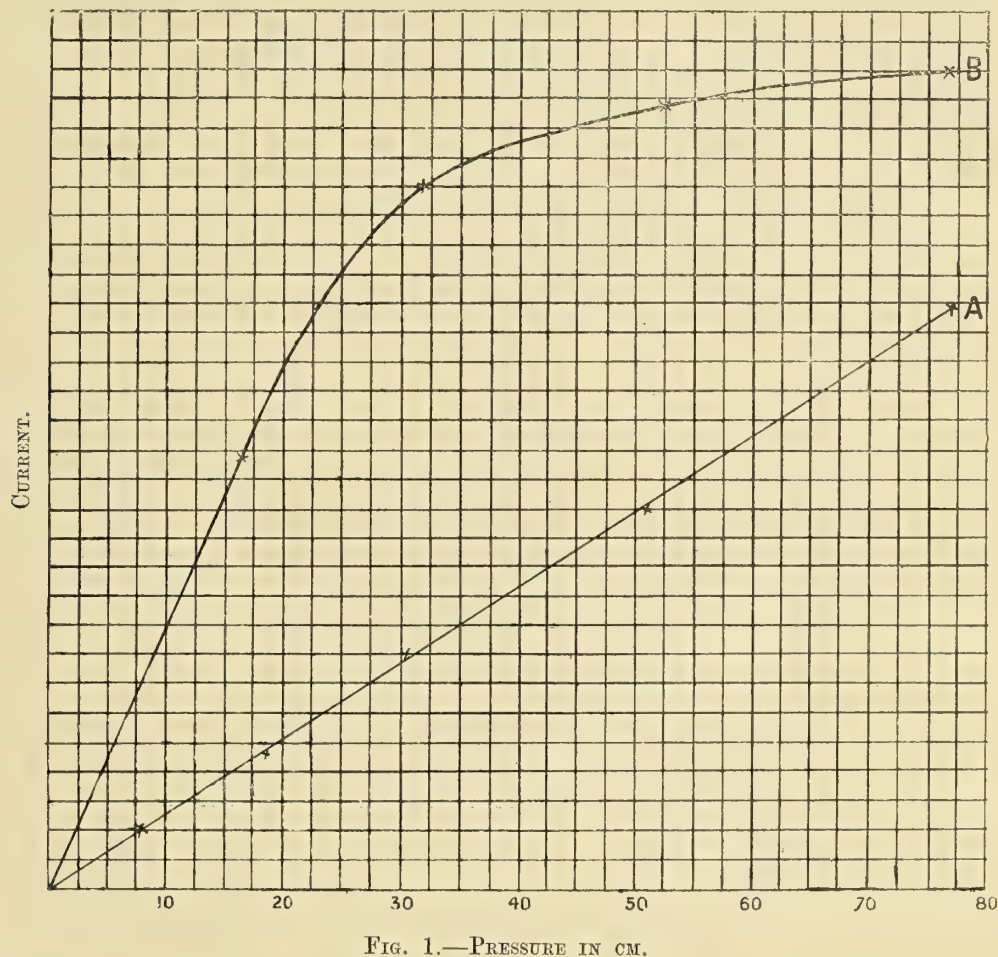
FIG. 1.—PRESSURE IN CM.

The result of one experiment is given as an example. Curve A, fig. 1, was obtained with the plates 4·5 cm. apart, the ionisation being produced by the direct β rays and the secondary radiation; there is no evidence whatever of the presence of any easily-absorbed radiation. Curve B on the same figure refers to an experiment with the plates the same distance apart, but the ionisation was produced by uranium oxide on the lower plate. The curve shows at once the presence of the easily-absorbed α rays which have been almost totally absorbed at about 35 cm. pressure.

We can conclude from these experiments that when β rays of radium fall on a metal plate no easily-absorbed secondary radiation—similar, say, to α rays—is produced.   By this conclusion we merely mean that no such radiation is produced comparable in intensity to the incident β rays.   We know from the work of various observers that substances, in general, spontaneously emit an easily-absorbed radiation of very weak intensity.   Our apparatus is not designed to detect such a very weak radiation, but merely to make certain that the penetrating secondary radiation studied in the previous papers, and which will be shown to be comparable in intensity to the incident β rays, is the only secondary radiation that we need consider when estimating the total energy of all the secondary effects.

It is perhaps worth mentioning that the method used in the above experiments was altered by keeping the pressure of the gas between the plates constant during an experiment, and having the lower plate so mounted that it could be gradually screwed away from the upper plate.   For small distances between the plates, the saturation-current might be expected to be proportional to the distance, provided there is no easily-absorbed radiation present.   This was not found to be the case, and the experiment seemed at first to indicate the presence of easily-absorbed radiation.   The method, however, fails for the following reason, and it affords an example of the errors that may arise from neglecting effects due to secondary radiation :—The penetrating radiation between the plates is not merely a cylindrical pencil perpendicular to the plates, and cannot be made so ; there are secondary rays travelling at all inclinations to the plates, so that, when the distance between the plates is increased, the path-lengths of all rays are not increased in the same ratio ; and the saturation-current is therefore not proportional to the distance.   This method of showing that a radiation is composed of two parts, one more easily absorbed than the other, is often employed ; but for the reason stated it is not reliable when any secondary radiation is produced.

DETERMINATION OF THE RATIO OF THE ENERGY OF THE SECONDARY RADIATION TO THAT OF THE PRIMARY RADIATION PRODUCING IT.

Having shown by the work in the previous papers, and the preliminary experiments in the present, that for all practical purposes the secondary radiation consists entirely of β rays very similar in every way to the incident β rays that produce them, we may therefore assume that the energy of the two radiations may be compared by measuring their ionising powers under similar conditions. It was only necessary to make this comparison for one substance, as the relative intensities of radiation from a large number of elements had been previously determined ; the substance used was lead.

Apparatus and Method of Experiment.

The radium R was placed as shown in fig. 2. P is the lead plate which was the source of the secondary rays; and it could be placed in position as shown, or removed when desired. When it was removed, the primary β rays passed into an ionisation-vessel consisting of a brass tube A, 20 cm. long and 7·5 cm. diameter, with an insulated brass rod B fixed along its axis and connected

FIG. 2

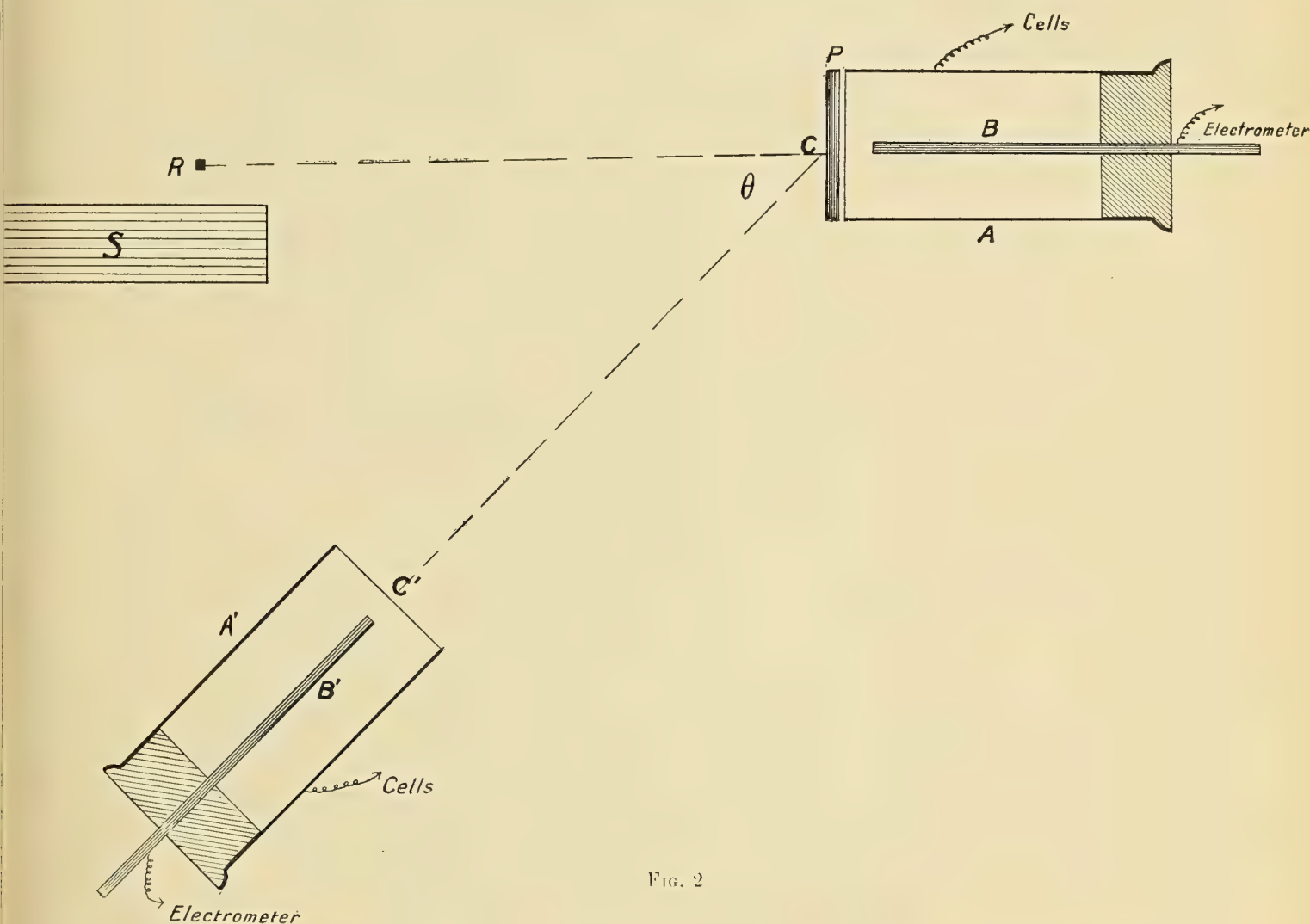to an electrometer. The end of the tube through which the radiation passes was covered with gold leaf. The tube was kept at a high potential, and the saturation-current to B measured in the usual way with the electrometer. The ionisation-vessel was then moved into the position A' such that CC' was equal to CR, and θ was 45°; and the lead plate P was placed as shown in the position

formerly occupied by the end of the tube A. The same pencil of rays that produced the ionisation measured in the first position of A was therefore used to produce secondary radiation from the plate P. The distance CC' was kept the same as CR, although not necessary for calculation-purposes, in order to ensure that the ionisation-chamber may really be similar in the two cases. In one case the pencil of rays falling on the end of the tube A diverges from the point R; and in the other case the rays diverge from all points of the plate P; it is therefore better to have the distances CC' and CR always equal, so that the pencil of rays entering the tube A may be equally effective in the two cases. S is a lead screen to protect the tube A' from direct radiation. In all observations corrections were applied for conductivity in the ionisation-chamber due to spontaneous ionisation or defective screening.

The secondary radiation is emitted in all directions from the plate, but not equally in all directions. An accurate determination was made of the ionisation produced in A' when θ was $45°$; and a separate investigation determined how the intensity of the radiation varied with θ; it will obviously, from symmetry, be constant while θ is constant. This separate investigation consisted in moving A' in one plane, changing θ and keeping CC' constant, and measuring the current for the different values of θ.

We give the numbers observed in one of many concordant determinations.

The ionisation produced by the primary β rays falling on A, the plate P being removed, gave a saturation-current measured by

<div align="center">246 scale-divisions per minute,</div>

the capacity charged being ·199 microfarads. When the plate P was in position, the saturation-current in A' was measured by

<div align="center">58 scale-divisions per minute,</div>

the capacity charged being ·01 microfarads. The area of the end of the ionisation tube A' was $\pi(3·75)^2$ sq. cm., and CC' was 20 cm.

Supposing for the moment that the secondary radiation from the plate P were the same in all directions, the ratio of the total energy of the secondary radiation to that of the primary would be

$$\frac{58 \times ·01}{246 \times ·199} \times \frac{2\pi(20)^2}{\pi(3·75)^2} = ·67.$$

A large number of observations similar to the above were made with the distance CC' (and CR), varying in different experiments from 30 cm. to 15 cm. They gave very concordant results, the mean of all the observations giving for the ratio the value ·68.

This result has finally to be corrected for the variation of the secondary radiation as the angle θ varies.

The saturation-current in A' was found to vary with θ as shown below:—

θ in Degrees.	Saturation-Current.
25	168
40	144
55	112
65	85
75	55
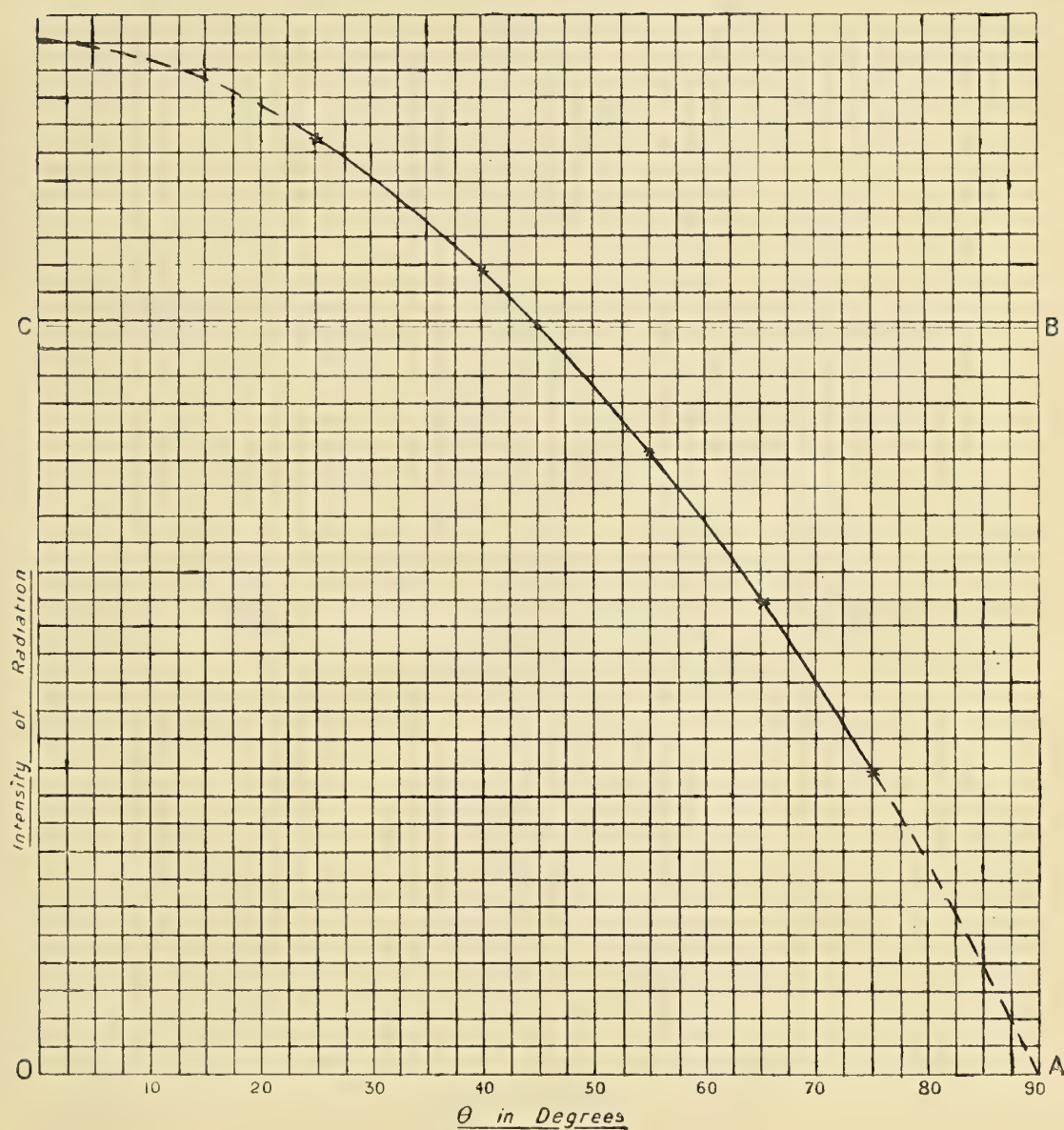
FIG. 3.

The curve in fig. 3 is plotted from the numbers. It was not convenient, on account of the size of the ionisation-tube A', to observe the current for

values of θ less than $25°$ or greater than $75°$; there can, however, be little error introduced by extending the curve to the axes, as is done in the figure, especially as the numbers observed showed that the intensity of the radiation varied very closely as $\cos \theta$.

The area of the portion of the surface of a sphere cut off by two coaxial cones of semi-angles θ and $\theta + d\theta$ is proportional to $\sin \theta \, d\theta$. Two curves (not shown in figure) were therefore plotted, one having for ordinates the ordinates of the given curve multiplied by $\sin \theta$, and the other having for ordinates the ordinate CO (corresponding to $45°$ on the given curve) multiplied by $\sin \theta$, the abscissæ in both cases being degrees from 0 to 90.

The ratio of the areas enclosed by these two curves and the axis was ·72.

Finally, therefore, the total energy of the secondary radiation from the lead plate bears to that of the primary radiation absorbed by the plate the ratio

$$\frac{·68 \times ·72}{1} = ·49.$$

The following table gives the value of this ratio (which we shall afterwards denote by p) in column IV. The numbers in column III. express, in an arbitrary scale, the secondary radiation from the different substances for the same amount of incident radiation absorbed; the numbers are copied from a previous paper.* The numbers in column IV. are calculated from column III., and the value of p found for lead above, viz. ·49.

The quantity κ, which is given in column V., is defined later in the paper.

The quantities p and κ are calculated in the table to the nearest half per cent.

* Royal Dublin Soc. Trans., Vol. ix., Part i.

TABLE I.*

I.		II.	III.	IV.	V.
SUBSTANCE.		Atomic Weight.	Secondary Radiation.	$p \times 100$.	$\kappa \times 100$.
Uranium,	. . . .	239·5	100	50·5	89
Bismuth,	. . . .	208·5	97	49	88·5
Lead, .	. . . .	206·9	97	49	88·5
Mercury,	. . . .	200·3	96	48·5	88
Platinum,	. . . .	194·8	93	47	87
Tungsten,	. . . .	184·0	88	44	85
Iodine,	. . . .	127·0	85·5	43	84
Antimony,	. . . .	120·0	85	42·5	83·5
Tin, .	. . . .	118·5	84	42·5	83·5
Cadmium,	. . . .	112·4	82	41·5	83
Silver,	. . . .	107·9	81	41	82·5
Molybdenum,	. .	96·0	78	39·5	80·5
Selenium,	. . . .	79·1	74	37	79
Arsenic,	. . . .	75·0	73	36·5	78·5
Zinc, .	. . . .	65·4	72	36·5	78·5
Copper,	. . . .	63·6	71	36	78
Cobalt,	. . . .	59·0	67	34	75·5
Nickel,	. . . .	58·7	67	34	75·5
Iron, .	. . . .	55·9	65	33	74·5
Chromium,	. . . .	52·1	63	31·5	73
Calcium,	. . . .	40·1	55	27·5	67·5
Potassium,	. . . .	39·1	54	27	67
Sulphur,	. . . .	32·06	53·5	27	67
Phosphorus,	. .	31·0	53	26·5	66
Aluminium,	. . .	27·1	48	24	62·5
Magnesium,	. .	24·4	43	21·5	58
Sodium,	. . . .	23·0	42	21·5	58
Carbon,	. . . .	12·0	29	15	45·5

*In abstracts of this paper previously published, values of p were quoted which were too large, the mistake arising from an arithmetical error in the calculations.

ANOTHER METHOD OF CALCULATING THE RATIO DENOTED BY p.

Some results recently published by Professor Righi[*] afford another method of calculating the ratio of the energy of the secondary radiation to that of the primary radiation. Righi allowed β rays to fall on a plate placed in a well-exhausted vessel, and connected to an electrometer. The plate got a negative charge; but the rate of charging was found to depend on the material of which the plate was made, although the same radiation was absorbed by the plate in each case. Righi found that the higher the atomic weight of the substance of which the plate was made the slower did it charge negatively, this result arising from the fact that the higher the atomic weight the greater the emission of secondary β particles.

Righi's paper gives the following numbers:—

Substance.	Negative Charge.
Carbon,	53
Aluminium,	46
Sulphur,	45
Iron,	43
Nickel,	41
Copper,	40
Zinc,	40
Silver,	33
Tin,	32
Platinum,	(21)
Lead,	26
Bismuth,	23

Now, if we let N denote the number of primary β particles falling on the plate in unit time, and if n_1 denote the number of secondary particles emitted when the plate is made of lead, we have

$$N - n_1 = 26a,$$

where a is some constant.

Similarly, if n_2 denotes the number of secondary particles emitted when the plate is made of, say, copper, we have

$$N - n_2 = 40a,$$

or

$$1 - \frac{n_1}{N} = \frac{26a}{N}$$

and

$$1 - \frac{n_2}{N} = \frac{40a}{N}.$$

But $\dfrac{n_1}{N}$ is the value of our ratio p for lead, and $\dfrac{n_2}{N}$ is the value for copper.

$$\therefore \frac{1 - p_1}{1 - p_2} = \frac{26}{40}.$$

In Column III. of Table I. we have the relative secondary radiations from lead and copper as measured by their ionising powers; from this column

$$\frac{p_1}{p_2} = \frac{97}{71}.$$

Combining this equation with the previous one we get

$$p_1 = \cdot66.$$

If we calculate the value of p for lead in this way, by taking lead with each of the other substances in Righi's table (omitting platinum, which is marked doubtful, and bismuth, which is too near to lead to give an accurate result), we get values for p lying between $\cdot60$ and $\cdot67$, and giving a mean value of $\cdot64$.

The agreement between the values of p for lead as calculated from Righi's results and as found above is not good. However, when we consider the widely different methods used, one comparing the radiations by measuring the ionisations produced, the other by measuring the charges carried, and as the leakage due to the ionisation of the residual gas surrounding the insulated plate in Righi's experiments must have been difficult to eliminate, we could scarcely expect a close agreement.

The Secondary Radiation from a Plate at Different Inclinations to the Normal.

Before leaving this part of the subject, we may very briefly refer to the way in which the intensity of the secondary radiation from the plate was found to vary with the inclination to the normal as shown in the previous

section, the exciting β rays falling normally on the plate. The numbers given above show that the secondary radiation in a direction inclined at an angle θ to the normal varies approximately as $\cos \theta$.

In a previous paper it was shown that, in the general case, there is a maximum secondary radiation in the direction fulfilling the laws of reflection; but the secondary radiation falls off unequally on the two sides of the maximum, the less rapid decrease occurring on the side nearer the normal.

In the section above, the conditions are simpler, as the incident radiation is normal to the plate. We get an explanation of the approximate $\cos \theta$ law by considering that the radiation travelling from any element at a small vertical depth d in the plate to an outside point in a direction θ from the normal has to pass through a thickness of the plate equal to

$$\frac{d}{\cos \theta},$$

and the intensity contributed by this element will therefore vary approximately as $\cos \theta$.

The whole question of the relation between the intensity of radiation and the direction, with respect both to the normal and to the direction of the exciting radiation, might repay further consideration.

Theoretical Investigation.

Having determined in a previous section the ratio (p) of the total energy of the secondary radiation from a thick plate to that of the exciting radiation, we can calculate what per cent. of the energy absorbed by any small element of volume of the plate is set free again as energy of secondary radiation.
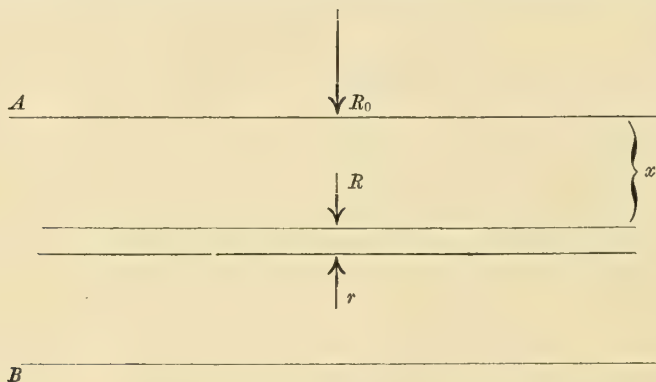
Let AB represent the plate, the exciting radiation falling normally on the face A.

Let the energy of the incident radiation passing through unit area of the face A per unit time be R_0.

Let the total downward flow of energy at depth x through unit area in unit time be R, and let the upward flow at same depth be r.

R is made up partly of unabsorbed primary radiation, and partly of secondary radiations, including under the term *secondary* not only true secondary radiation, but also tertiary and all successive radiations. The upward flow r is composed entirely of secondary radiations. Further, let μ denote what the coefficient of absorption would be if there were no secondary radiations, and let κ denote the ratio of the energy of the secondary radiation given out by the layer dx to the incident energy absorbed by this layer.

With this notation we have

$$\frac{dR}{dx} = -\mu R + \frac{\mu\kappa}{2} R + \frac{\mu\kappa}{2} r.$$

The first term on the right-hand side results from the absorption of primary radiation; the second term expresses that κ times the energy absorbed is set free again as secondary radiation, of which, as an approximation, half may be taken as travelling upwards and half downwards. The third term results from the fact that, in the layer considered, the quantity μr of the upward flow is absorbed with a corresponding generation of secondary. The coefficient μ is taken to be the same for all the radiations primary and secondary.

In exactly the same way we have

$$-\frac{dr}{dx} = -\mu r + \frac{\mu\kappa}{2} r + \frac{\mu\kappa}{2} R,$$

or

$$\frac{dR}{dx} = -aR + br \qquad (1)$$

and

$$\frac{dr}{dx} = ar - bR \qquad (2)$$

where

$$a = \mu\left(1 - \frac{\kappa}{2}\right)$$

and

$$b = \frac{\mu\kappa}{2}$$

From (1) and (2) we get

$$\frac{d^2 R}{dx^2} = (a^2 - b^2)\,R$$

and

$$\frac{d^2 r}{dx^2} = (a^2 - b^2)r.$$

In our problem we know that thick plates absorb the radiation completely, so that we are not concerned at present with the periodic solution corresponding to negative values of

$$a^2 - b^2.$$

For positive values we must have

$$b < a, \qquad \text{or} \qquad \frac{\mu\kappa}{2} < \mu\left(1 - \frac{\kappa}{2}\right), \qquad \text{or} \qquad \kappa < 1.$$

The energy set free as secondary radiation from any element of volume cannot therefore exceed the incident energy absorbed by the element.

For values of κ less than unity we have

$$R = Ae^{-x\sqrt{a^2 - b^2}} + A'e^{x\sqrt{a^2 - b^2}},$$

and

$$r = Be^{-x\sqrt{a^2 - b^2}} + B'e^{x\sqrt{a^2 - b^2}}.$$

Taking, in the first place, an infinitely thick plate, which, for our purpose, need only be a plate thick enough to transmit no radiation, we have

$$A' = 0, \qquad B' = 0, \qquad \text{and} \qquad A = R_0;$$

and from equation (1) we get

$$B = \frac{a - \sqrt{a^2 - b^2}}{b} R_0.$$

Therefore

$$R = R_0 e^{-x\sqrt{a^2 - b^2}},$$

and

$$r = \frac{a - \sqrt{a^2 - b^2}}{b} R_0 e^{-x\sqrt{a^2 - b^2}}.$$

Now p is equal to

$$\frac{r}{R}, \quad \text{when} \quad x = 0;$$

$$\therefore \qquad p = \frac{a - \sqrt{a^2 - b^2}}{b}.$$

Substituting for a and b,

$$p = \frac{1 - \dfrac{\kappa}{2} - \sqrt{1 - \kappa}}{\dfrac{\kappa}{2}},$$

or

$$\kappa = \frac{4p}{(p + 1)^2}.$$

The column headed κ in Table I. has been calculated from this result by substituting the known values of p for the different substances. It will be noticed that as much as $88\frac{1}{2}$ per cent. of the incident energy absorbed by any element of a lead plate is set free again as secondary radiation, the corresponding number for uranium being 89 per cent., and for the element of lowest atomic weight tested, carbon, the percentage is 45.

For values of p in the neighbourhood of ·5 κ varies very slowly as p varies, so that an error in determining p for lead (the substance used) would not produce much effect on the calculated values of κ. When the secondary radiation from different elements was plotted against the atomic weight in the previous paper, the substances fell into well-defined divisions, corresponding to the chemical *periods*; this plotting was the same as plotting p against the atomic weight. Now κ is a more fundamental constant than p, and might be expected to bring out more clearly the divisions referred to; but this advantage is counterbalanced by the fact that the total variation of κ is less than that of p. When κ is plotted against the atomic weight, the divisions corresponding to the chemical *periods* are clearly shown, but no better than in the previous paper, where p was used.

Some Deductions from the above Results.

The fact that such a large percentage of the energy of the radiation absorbed by any element of volume is set free again as secondary radiation has very important bearings in many directions.

Consider, in the first case, the rate of absorption of β rays by a *thick* plate of a substance. The true coefficient of absorption of the actual β particles incident on the plate is the quantity μ in the above equations; the coefficient of absorption of the total radiation passing through the plate, partly primary and partly secondary, is not μ, but is

$$\sqrt{a^2 - b^2}, \qquad \text{or} \qquad \mu\sqrt{1 - \kappa}.$$

In the case of lead, for example, κ is about ·88, so that the actual coefficient of absorption for lead is only one-third of what the coefficient would be if there were no secondary radiation. In other words, the average distance to which the incident β particles penetrate into the lead is only one-third of the distance they appear to penetrate, due to the successive generation of other β particles.

Further, in the usual method of determining the coefficient of absorption, the intensity of the radiation is measured in some way; then a plate of the

substance interposed, and the intensity again measured after passing through the plate. A coefficient of absorption is then calculated by assuming

$$R_d = R_0 e^{-\lambda' d},$$

where R_d is the intensity of radiation after traversing the plate of thickness d, R_0 is the incident radiation, and λ' is the coefficient of absorption. This method does not give the coefficient of absorption accurately; too great a value will be found when the thickness of the absorbing layer is very small, and the error will be greater in the case of substances which give strong secondary radiation. The coefficient determined in this way should diminish as the thickness of the absorbing layer increases, even in the case of a perfectly homogeneous radiation. The coefficient of absorption of β rays determined in this way has been found to decrease rapidly as the thickness traversed increases; and the result has been taken to show the marked heterogeneity of the rays as regards penetrating power. Part of the observed decrease of the coefficient, but not all of it, is, however, due to the faultiness of the method, so that the rays are not so heterogeneous as such experiments might indicate. We see this as follows :—

Using the notation of the previous section, the intensity of the downward flow of energy at depth x of a plate which is not thick enough to prevent all transmission of radiation is

$$R = A e^{-x\sqrt{a^2-b^2}} + A' e^{x\sqrt{a^2-b^2}}.$$

We shall write λ for

$$\sqrt{a^2 - b^2} \; ;$$

and our object is to show how λ differs from λ', determined as described above, and how the difference depends on the thickness d of the plate used.

When $\qquad\qquad x = 0,$

we have $\qquad\qquad R_0 = A + A';$

$$\therefore \quad R = R_0 e^{-\lambda x} + A'(e^{\lambda x} - e^{-\lambda x}).$$

Using the equation (1) above, viz. :

$$\frac{dR}{dx} = -aR + br,$$

and remembering that $r = 0$, when $x = d$, we get

$$(\lambda - a) R_0 e^{-\lambda d} = A' \{(\lambda + a) e^{\lambda d} + (\lambda - a) e^{-\lambda d}\},$$

and

$$R_d = R_0 e^{-\lambda d} + A' (e^{\lambda d} - e^{-\lambda d}).$$

Eliminating A' we get

$$\frac{R_0}{R_d} = \frac{(\lambda + a) e^{\lambda d} + (\lambda - a) e^{-\lambda d}}{2\lambda}.$$

But

$$\frac{R_d}{R_0} = e^{-\lambda' d}.$$

$$\therefore \quad e^{\lambda' d} = \frac{1}{2\lambda} \{(\lambda + a) e^{\lambda d} + (\lambda - a) e^{-\lambda d}\},$$

or

$$e^{\lambda' d} = C e^{\lambda d} - (C - 1) e^{-\lambda d}, \qquad (3)$$

where

$$C = \frac{\lambda + a}{2\lambda} = \frac{\sqrt{a^2 - b^2} + a}{2\sqrt{a^2 - b^2}} = \frac{\sqrt{1 - \kappa} + \left(1 - \dfrac{\kappa}{2}\right)}{2\sqrt{1 - \kappa}}.$$

C can be calculated for any substance from the value of κ given in Table I.

From equation (3) we see that $\lambda' = \lambda$ when d is [ ] and $\lambda' = (2C - 1)\lambda$ when d is infinitely small.

It follows, therefore, that when the coefficient of absorption i[ ] the way described, different values should be found according to [ ] substance used even when the radiation is perfectly homogeneous. C depends on the value of κ for the substance used; substituting from Table I., we find that C varies from 1·32 for lead to 1·02 for carbon. The maximum value of λ' for lead is therefore 1·64λ, and for carbon 1·04λ.

Tin is often used in determinations of the absorption coefficient, as it can easily be obtained in thin sheets. The value of λ' for tin for different values of d has been calculated from equation (3), giving λ the constant value 100. The result is shown in the following table, the maximum value of λ' being 144 :—

Thickness of tin in mm.	λ'.
·01	140
·05	126
·10	117
·20	110
·30	106
·50	103

It follows from these numbers that the β rays of radium are not so

heterogeneous as the experiments on their absorption by matter, made in the usual way, would indicate. Still, a comparison of the above table with the results of such experiments shows that after we have corrected for the error in the experiments introduced by the secondary effects, there is left a considerable decrease of the absorption coefficient as the thickness of the substance traversed increases.

It is hoped to publish shortly further results on the passage of β radiation through matter.

In conclusion, I have much pleasure in thanking Mr. F. E. Hackett, M.A., for valuable assistance in the work described in this paper.

TRANSACTIONS (SERIES II.).

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IN previous papers* one of the present authors has studied, in considerable detail, the secondary radiation of β particles which is emitted by substances when they are exposed to the β (and γ) rays of radium. The intensity of this secondary radiation was measured in the case of a large number of elementary substances, and, as shown in the papers referred to, it was found that the intensity of the radiation depended on the atomic weight of the element. The secondary radiation is greater the greater the atomic weight, and increases with the atomic weight in such a way as to lead to an arrangement of the elements in divisions exactly corresponding to the division into *periods* employed in chemistry. In the previous papers the theory was advanced that the action producing the secondary radiation is entirely an atomic one. It was held that the electrical disturbance produced by the primary β particles penetrating the atoms of the substances exposed to them caused some of the atoms to break up, thus producing the emission of secondary β particles. The electric forces in the γ-ray pulse will, obviously, act similarly to the electrical forces due to the penetration of the β particles, so that the γ rays produce this secondary radiation as well as the β rays. If the emission of the secondary radiation is entirely an atomic property, it should be possible to calculate the intensity of the radiation given by a chemical compound, provided we know the radiating power of each of its constituents and the relative amounts of each present in the compound.

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* Trans. Roy. Dublin Soc., vol. viii., part xiv , 1905; vol. ix., part i., 1905; and vol. ix., part ii., 1906.

In this paper the secondary radiation from a number of compounds has been measured experimentally, and compared with the value calculated on the lines mentioned above. It may be stated at once, that the calculated and the
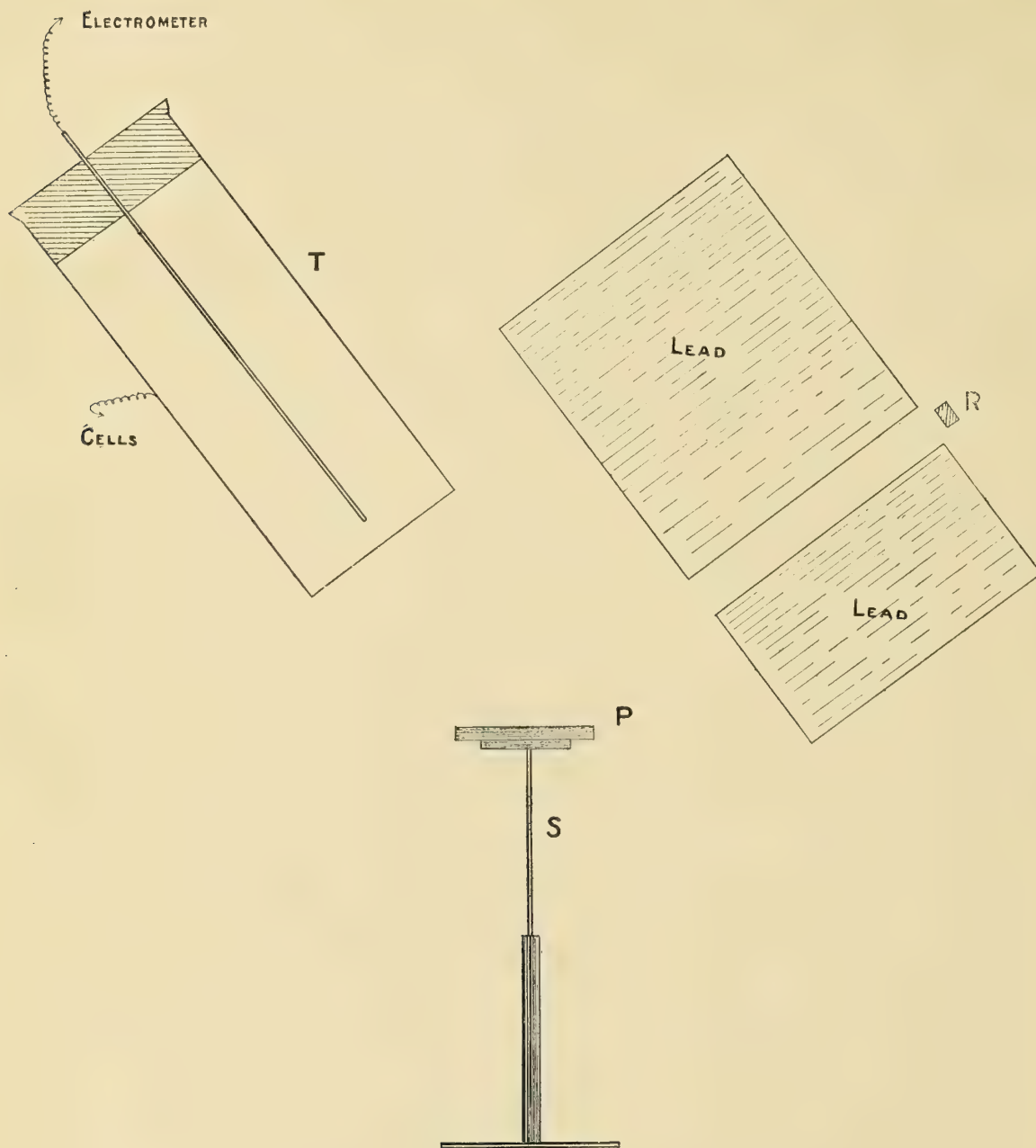

Fig. 1.

experimental values show very good agreement, and thus confirm the theory that the action is an additive atomic property.

Apparatus for the Experimental Determination.

The apparatus used was the same as in the later determinations of the radiations from elementary substances, but for convenience it may be briefly described here :—

The radium is placed at R (fig. 1) so that a stream of β (and γ) rays passes through a hole in a thick lead screen and falls on P, the substance under examination, which is generally in the form of a fine powder contained in a small mica vessel resting on the support S.

The secondary radiation which is emitted by the substance P in all directions, is measured by the ionisation it produces in the vessel T; this is a brass tube of 20 cm. length and 7·5 cm. internal diameter, the end towards P being covered with a sheet of tinfoil. An inner terminal, insulated by a paraffin cork, is fixed along the axis of T and joined to a sensitive electrometer; T is kept at a high potential and the ionisation is measured in the usual way by the rate of charging of the inner terminal.

The distance from R to P is about 25 cm., and from P to the tube T about 9·5 cm. The vessel containing the radium and the air space between it and the substance at P absorb all the α rays and the more easily absorbed β rays, so that the radiation acting on the substance consists chiefly of β rays with some γ rays. In every case the upper surface of the substance under examination was placed in exactly the same position, and a sufficient thickness was used in each case to absorb all the incident β rays, so that the incident energy absorbed was the same for each substance tested. Of course corrections were always applied for whatever small ionisation existed inside T when the substance P was removed and the stand S lowered.

Method of Calculating Theoretically the Secondary Radiation from a Compound.

In one of the previous papers* referred to above, the secondary radiation from a large number of elements was determined, the intensity of the secondary radiation being expressed as a percentage of the primary radiation that produced it, the thickness of substance used in every case being great enough to allow of no transmission of β rays. This percentage we shall denote by the letter p, as in the previous paper.

In that paper another constant for each element was deduced theoretically from the known value of p; this constant was denoted by κ, and expressed the ratio

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* Trans. Roy. Dublin Soc., vol. ix., part ii., 1906.

of the energy emitted as secondary β particles by any small volume of the substance to the energy of the primary radiation absorbed by that volume. The relation between these two constants was shown to be

$$\kappa = \frac{4p}{(p+1)^2}$$

and from the observed values of p, the values of κ were calculated by this equation.

Consider now the absorption of a compound, and the emission of secondary radiation from it.

If we let R denote the energy passing per unit time through unit area of a surface at depth x in the compound, the part of this energy absorbed in a thickness dx is $\mu R dx$, and the corresponding amount of energy set free again as secondary β rays from the layer is $\mu \kappa R dx$, where μ is the true coefficient of absorption of the compound for the radiation, and κ is the transformation-constant of the compound as defined above.

If now the absorption and emission of secondary rays are atomic properties, we can consider the total absorption and emission as the sum of the absorptions and emissions of the separate atoms, the atoms of different types having different values for μ and κ.

If there are n_1 atoms of any class in unit volume, and if the average absorption produced by each atom of this class is a_1, we have therefore

$$\mu = \Sigma n_1 a_1$$

and

$$\mu \kappa = \Sigma n_1 a_1 \kappa_1 ;$$

and therefore

$$\kappa = \frac{\Sigma n_1 a_1 \kappa_1}{\Sigma n_1 a_1}.$$

Again, we have obviously

$$a_1 = \frac{\mu_1}{N_1}$$

where μ_1 is the true coefficient of absorption of an elementary substance composed of atoms of the class to which a_1 refers, and N_1 is the number of atoms in unit-volume of this element.

Further, if d_1 denote the density of this elementary substance, and w_1 its atomic mass, we have

$$N_1 w_1 = d_1.$$

Therefore

$$a_1 = \frac{\mu_1 w_1}{d_1} ;$$

and therefore
$$\kappa = \frac{\Sigma n_1 w_1 \dfrac{\mu_1}{d_1} \kappa_1}{\Sigma n_1 w_1 \dfrac{\mu_1}{d_1}} \; ;$$

or finally
$$\kappa = \frac{\Sigma m_1 \dfrac{\mu_1}{d_1} \kappa_1}{\Sigma m_1 \dfrac{\mu_1}{d_1}} \; ,$$

where m_1 is the mass of any element per unit volume of the compound, and μ_1, d_1, and κ_1 are the true coefficient of absorption, density, and transformation-constant of that element.

Before we can use this expression to enable us to calculate κ for a compound, we must know the true coefficient of absorption (μ) for the constituents of the compound. In a previous paper,* by one of us, the relation between μ and the usually observed coefficient was worked out; but it was also shown that the methods hitherto employed in measuring the coefficient of absorption involved considerable inaccuracies owing to the fact that the effects of secondary radiation had always been neglected. We have not, therefore, the data necessary to supply accurate values of μ for the elements.

An approximation to accuracy will be to take μ to be proportional to the density d of the elementary substance. With this assumption the expression giving κ for a compound takes the simple form—

$$\kappa = \frac{\Sigma m_1 \kappa_1}{\Sigma m_1}.$$

From some work going on in this laboratory at present, it is probable that the ratio μ/d will be found to increase with the atomic weight of the substance. If so, since κ for all elements increases as the atomic weight increases, calculations made from the above simple expression should give too small a value for κ for a compound in which an element of high atomic weight is combined with one of low atomic weight. It should give an accurate result for compounds composed of elements of nearly equal atomic weights. The error introduced should, in any case, always be small, because of the form in which $\dfrac{\mu}{d}$ occurs in the expression for κ. This is practically what has been found to occur, as will appear from the results shown in the following table. The differences between the calculated and the observed values are always small, and in the cases in which the difference is appreciable the compound is made up of elements of very different atomic weights, and the calculated value is less than the observed value.

* Trans. Roy. Dublin Soc., vol. ix., part ii., 1906.

As it is the constant p, and not κ, which is measured directly in the experiments, the values of p have been given in the table. As stated earlier in this paper, the relation between p and κ is—

$$\kappa = \frac{4p}{(p+1)^2}.$$

In calculating κ for a compound, the values of κ for its constituents are taken from the table given in the previous paper referred to above. Chlorine and oxygen, which occur as constituents in some of the compounds tested, are not included among the elements examined in the previous paper; but sufficient other elements of neighbouring atomic weights are included to enable the value of κ for these elements to be fixed with accuracy.

Table.

Substance.	$p \times 100$ calculated.	$p \times 100$ observed.
HgI_2, . . .	45·5	46·5
BiI_3, . . .	45	46·5
CdI_2, . . .	42·5	42·5
KI, . . .	38	38·5
PbS, . . .	45	46
HgS, . . .	44	46
Bi_2S_3, . . .	43	46·5
SnS, . . .	38	38·5
Sb_2S_3, . . .	36·5	37·5
ZnS, . . .	33	34
CuS, . . .	33	33
CaS, . . .	27	27·5
HgCl, . . .	44	46·5
$HgCl_2$, . . .	41	42
PbO, . . .	45	47·5
PbO_2, . . .	42	46
SnO, . . .	38	39
ZnO, . . .	31·5	34
CuO, . . .	31	32

Further Determinations for Compounds.

The results given in the above table show clearly that the emission of secondary radiation of the β-ray type is an additive atomic property, and can be calculated for any molecule when we know the radiating powers of its constituents.

In addition to the examination of the compounds contained in this table, a number of other determinations were made. In the first place, some compounds rich in hydrogen, such as water, toluene, benzene, and aniline, were tested in order to determine the radiating power of hydrogen, the element of lowest atomic weight. In these determinations the value of κ for the compound and for its constituents, other than hydrogen, was known, and the value for hydrogen could therefore be calculated. This method was justified, since the previous results showed that the property under examination was strictly additive. Some of the compounds tested gave a very small positive value of κ for hydrogen, while others gave a small negative value, showing that the true value for hydrogen was too small to be measured accurately by this method. This is exactly what was to be expected from the results in the previous paper, which showed that the secondary radiation from elements diminishes as the atomic weight diminishes.

Since the compounds hitherto examined had a rather simple molecular structure, a few very complex compounds were examined, such as potassium ferrocyanide, potassium ferricyanide, and chrome alum. In every case the agreement between the observed and the calculated values was quite as good as in the case of the simple compounds contained in the above table.

Another application of the results in this paper has reference to the previous work by one of us on the variation of the secondary β radiation with the atomic weight. It was shown in the previous paper that while the secondary radiation always increases when the atomic weight increases, the rate of increase is such as to give a division of the elements exactly corresponding to the division into "periods" employed in chemistry. Among the elements previously tested, all the chemical periods were represented except the one containing barium, cerium, didymium, &c. On account of the difficulty of obtaining these elements in sufficient quantity in the pure state, none of them were previously tested. It is now possible to calculate the secondary radiation for the element, knowing it for a compound containing the element and for the other constituents. Experiments have therefore been made with compounds of barium, cerium, and didymium. The curves given in the previous paper, and which are repeated below (fig. 2), showed that as we pass along a chemical period in the direction of increasing atomic weight, there is a rapid increase of secondary radiation, with a marked

change of slope as we pass from one period to the next. At first sight these curves indicate a possible peculiarity for the period containing barium, inasmuch as the secondary radiation from the last element (iodine) of the preceding period is very little less than that from the first element tested (tungsten) in the following period.

If, therefore, the elements of the period containing barium are to take their place in the general scheme, little room is left for increase of secondary radiation as we pass along this period in the direction of increasing atomic weight. This is exactly the result indicated by the comparatively few determinations we have been able to make for barium, cerium, and didymium. There is scarcely any difference between the secondary radiations from the elements of this period; but the period as a whole takes what is its proper place according to the previous results. On the same scale as that employed in fig. 2, the values found for barium, cerium, and didymium, are 86, 86·5, and 86·5, respectively. This period as a whole, therefore, does not present any exception to the general rule that the secondary radiation increases as the atomic weight increases; but it is different from the other chemical periods, inasmuch as there is not a marked increase of secondary radiation as we pass along the period in the direction of increasing atomic weight.

In discussing the results in the previous paper from the point of view that the atoms of all elements are composed of electrons, it was pointed out that as we go from one element to another of greater atomic weight in the same period, the additional electrons necessary to form the heavier atom are added on in a way that increases considerably the secondary radiation; but in passing from one period to the next, the additional electrons must be added on in some different way which is not so effective in increasing the secondary radiation, thus producing the change of slope in passing from one period to the next. Also, since the chemical properties change from element to element in any period, we see that the method of adding on additional electrons which produces a rapid increase of secondary radiation also produces a marked change of chemical properties. From this point of view the behaviour of the period containing barium is very interesting. Here we have an exception to what happens in the case of the other periods; in this period there is practically no increase of secondary radiation from element to element. But from the chemical point of view, this period presents an exactly parallel exception; in this period there is so little difference in the chemical properties of the different elements that it is difficult to separate them.

As the only element in the first chemical period previously tested was carbon, some further determinations were made with compounds in the same way as above, in order to fix the slope of the curve corresponding to this period.

Fig. 2

Atomic Weight

Secondary Radiation
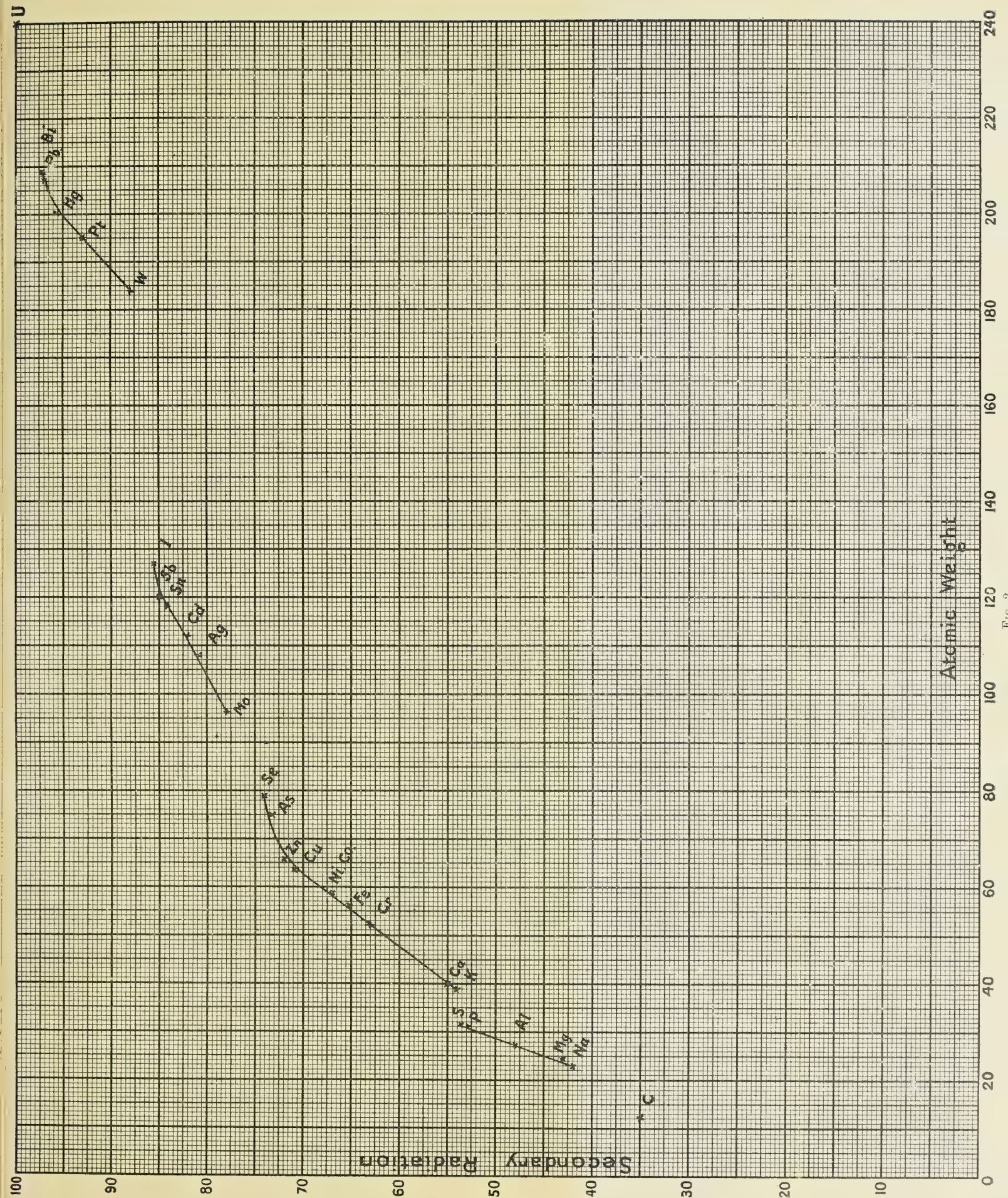
Carbon was again tested, using a pure sample, and it was found necessary to appreciably reduce the value of the secondary radiation given in fig. 2. The general result of the determinations made for elements in this period was to show that the part of the curve corresponding to this period is steeper than for any other period. This again is in complete accord with the fact that the change in chemical properties from element to element in this period is more marked than in any other period.

General Discussion.

The work in this paper, together with that in the previous papers referred to, shows very clearly that the property dealt with is entirely an atomic one, and that the secondary β radiation excited by an incident radiation of constant intensity depends in a remarkable way on the atomic weight of the element concerned. In a previous paper a general theory was sketched of how this connection may arise, and of the possible meaning of the divisions of the elements corresponding to the chemical periods, but the present is a suitable occasion to add a few more remarks on the subject.

Whether the emission of these secondary β rays involves a breaking up of the atom in the sense that we use the term in connection with radio-activity is a point that is not decided. In the previous paper the energy of the secondary radiation was compared with that of the primary producing it, and from these determinations a theoretical calculation enabled it to be shown that of the energy absorbed by any element of volume of a substance as much as 89·5 per cent. was emitted again as *secondary β rays* in the case of lead, the percentage being, of course, even slightly greater for bismuth and uranium, the only substances tested of higher atomic weight. From this result, and the method of calculation used, it is easy to see that an exceedingly small emission *from* a plate of lead of very easily absorbed secondary radiation would lead to the result that the energy of the total secondary radiation from any element of *volume in* the plate would exceed the energy of the radiation absorbed by that element of volume. Such a conclusion would, of course, prove that the effect was of the nature of true radio-activity; and, moreover, would be an example of radio-activity artificially controlled. However, it must be stated that we have for so far no proof that there is this additional quantity of easily-absorbed secondary radiation. It is, of course, possible that the emission of the β particles which constitute the secondary radiation does not follow from, or result in, a breaking up of the atom in the sense that we use the term in radio-activity. The β particles that are emitted as secondary radiation must, however, actually come from the

atoms ; if they were free electrons just before emission, it is difficult to see how such remarkable relations should exist between the atomic weight and the intensity of the secondary radiation.

It may be mentioned in conclusion that the further measurements of this secondary radiation treated of in this paper confirm our previous belief as to the small difference of atomic weight that can be detected by the corresponding difference in intensity of the radiation.   At a part of the curves (fig. 2) where the secondary radiation is increasing most rapidly a difference of one unit in atomic weight would readily be detected by the difference in the secondary radiation.

TRANSACTIONS (SERIES II.).

VOLUME IX.

Part

1. On Secondary Radiation (Part II.), and Atomic Structure. By J. A. McClelland, M.A., Professor of Experimental Physics, University College, Dublin. (May 17, 1905.) 1s.

II. The Energy of Secondary Radiation. By J. A. McClelland, M.A., Professor of Experimental Physics, University College, Dublin. (February 6, 1906.) 1s.

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VOLUME IX.—(SERIES II.)

IV.

THE ABSORPTION OF β RADIUM RAYS BY MATTER.

BY

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Professor of Experimental Physics, University College, Dublin;

AND

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IV.

THE ABSORPTION OF β RADIUM RAYS BY MATTER.

By J. A. McCLELLAND, M.A., D.Sc.,

Professor of Experimental Physics, University College, Dublin ;

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F. E. HACKETT, M.A., B.Sc.

THE emission of secondary β particles from matter traversed by β radium rays has been investigated in considerable detail by one of us, and the result has been established that the intensity of this secondary radiation from any element depends on its atomic weight. The secondary radiation increases as the atomic weight increases ; the rate of increase with atomic weight is not uniform, and the form of the curve connecting the intensity of the secondary radiation with the atomic weight of the element is such as to establish a division of the elements exactly corresponding to the division into *periods* employed in chemistry. The details of this work and its bearing on the question of atomic structure have been described and discussed in previous papers.*

The intensity of this secondary radiation being found to depend so markedly on the atomic weight of the substance acted upon by the primary β rays, suggests that the coefficient of absorption of substances for β radiation may also be dependent on the atomic weight. This coefficient is of course known to be roughly proportional to the density ; the division of the coefficient by the density is necessary to give the same relative amounts of matter traversed in the different cases. The object of the present work is rather to study the variation of the ratio of the absorption coefficient to the density in the hope that this line of work would yield further results bearing on atomic structure of a character similar to those contained in the previous work.

* Trans. Roy. Dublin Soc., vol. viii., part xiv., 1905 ; vol. ix., part i., 1905 ; vol. ix., part ii., 1906 ; and vol. ix., part iii., 1906.

The previous work above referred to has shown that accurate values of the coefficient of absorption of β radium rays cannot be obtained unless the effects due to secondary radiation are taken into account. This was shown incidentally in a previous paper,[*] but the theoretical investigation required for the present work is given fully here.

Let AB represent a plate through which β rays are passing.
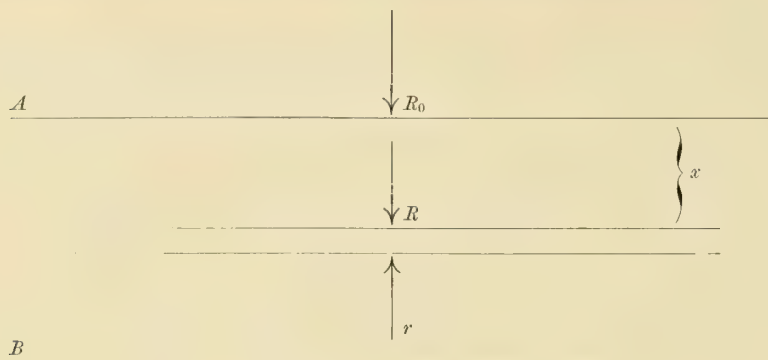
Let the energy of the incident radiation passing through unit area of the face A per unit time be R_0.

Let the total downward flow of energy at depth x through unit area in unit time be R, and let the upward flow at same depth be r.

R is made up partly of unabsorbed primary radiation, and partly of secondary radiations, including under the term *secondary* not only true secondary radiation, but also tertiary and all successive radiations. The upward flow r is composed entirely of secondary radiations.

Now let μ denote what the *true* coefficient of absorption would be if there were no secondary effects, and let κ denote the ratio of the energy of the secondary radiation given out by the layer dx to the incident energy absorbed by this layer.

With this notation we have

$$\frac{dR}{dx} = -\mu R + \frac{\mu\kappa}{2} R + \frac{\mu\kappa}{2} r.$$

The first term on the right-hand side results from the absorption of primary radiation; the second term expresses that κ times the energy absorbed is set free again as secondary radiation, of which, as an approximation, half is taken as travelling upwards and half downwards. The third term results from the fact that, in the layer considered, the quantity μr of the upward flow is

* Trans. Roy. Dublin Soc., vol. ix., part ii., 1906.

absorbed with a corresponding generation of secondary. The coefficient μ is taken to be the same for all the radiations primary and secondary; this assumption is justified by previous work.

In exactly the same way we have

$$-\frac{dr}{dx} = -\mu r + \frac{\mu \kappa}{2} r + \frac{\mu \kappa}{2} R,$$

or

$$\frac{dR}{dx} = -aR + br \qquad (1)$$

and

$$\frac{dr}{dx} = ar - bR \qquad (2)$$

where

$$a = \mu \left(1 - \frac{\kappa}{2} \right)$$

and

$$b = \frac{\mu \kappa}{2} \, .$$

From (1) and (2) we get

$$\frac{d^2 R}{dx^2} = (a^2 - b^2) \, R,$$

$$\frac{d^2 r}{dx^2} = (a^2 - b^2) \, r.$$

For values of κ less than unity we have

$$R = A e^{-x \sqrt{a^2 - b^2}} + A' e^{x \sqrt{a^2 - b^2}},$$

and

$$r = B e^{-x \sqrt{a^2 - b^2}} + B' e^{x \sqrt{a^2 - b^2}} .$$

For a plate thick enough to transmit no radiation, we have

$$R = R_0 e^{-x \sqrt{a^2 - b^2}} .$$

The coefficient of absorption of the total radiation passing through the plate, partly primary and partly secondary, is

$$\sqrt{a^2 - b^2} \quad \text{or} \quad \mu \sqrt{1 - \kappa}.$$

The *true* coefficient of absorption for any specified set of particles is the quantity μ.

We must carefully distinguish between these two coefficients ; and it is obvious that in studying the stopping power of different substances or different forms of atoms we should deal with the coefficient μ and not with the different coefficient

$$\mu\sqrt{1-\kappa},$$

the value of which depends on the efficiency of the substance as a source of secondary radiation.

The value of κ for a large number of elements was determined in a previous paper* dealing with secondary radiation, so that all we require to do is to find the coefficient $\mu\sqrt{1-\kappa}$ accurately. Experiments of the usual type dealing with absorption do not, however, give an accurate value of this coefficient. In the usual method of determining the coefficient of absorption, the intensity of a pencil of rays is measured, and then a plate of the substance under investigation is interposed, and the intensity again measured. The quantity λ' which satisfies the equation

$$R_d = R_0 e^{-\lambda' d}$$

is then calculated, where R_d is the intensity after traversing the plate of thickness d, R_0 is the incident radiation, and λ' is called the coefficient of absorption. The quantity λ' refers to the total radiation, primary and secondary, but it is not the same as our coefficient

$$\mu\sqrt{1-\kappa},$$

and in fact the value of λ' depends on the thickness of plate used even when the radiation is perfectly homogeneous.

This is easily seen as follows:—

We have as above

$$R = Ae^{-x\sqrt{a^2-b^2}} + A'e^{x\sqrt{a^2-b^2}},$$

or writing λ for $\sqrt{a^2-b^2}$

$$R = Ae^{-\lambda x} + A'e^{\lambda x}.$$

We can show that λ' differs from λ, and that the difference depends on the thickness d of the plate used to absorb the rays.

When $x = 0,$ we have $R_0 = A + A'$;

$$\therefore \quad R = R_0 e^{-\lambda x} + A'(e^{\lambda x} - e^{-\lambda x}).$$

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* Trans. Roy. Dublin Soc., vol. ix., part ii., 1906.

Using the equation (1) above, viz. :

$$\frac{dR}{dx} = -aR + br,$$

and remembering that $r = 0$ when $x = d$, we get

$$(\lambda - a) R_0 e^{-\lambda d} = A'\{(\lambda + a) e^{\lambda d} + (\lambda - a) e^{-\lambda d}\},$$

and

$$R_d = R_0 e^{-\lambda d} + A'(e^{\lambda d} - e^{-\lambda d}).$$

Eliminating A' we get

$$\frac{R_0}{R_d} = \frac{(\lambda + a) e^{\lambda d} + (\lambda - a) e^{-\lambda d}}{2\lambda}.$$

But

$$\frac{R_0}{R_d} = e^{\lambda' d};$$

$$\therefore \quad e^{\lambda' d} = \frac{1}{2\lambda}\left\{(\lambda + a) e^{\lambda d} + (\lambda - a) e^{-\lambda d}\right\},$$

or

$$e^{\lambda' d} = C e^{\lambda d} - (C - 1) e^{-\lambda d}, \qquad (3)$$

where

$$C = \frac{\lambda + a}{2\lambda} = \frac{\sqrt{a^2 - b^2} + a}{2\sqrt{a^2 - b^2}} = \frac{\sqrt{1 - \kappa} + \left(1 - \dfrac{\kappa}{2}\right)}{2\sqrt{1 - \kappa}}.$$

C can be calculated for any substance from the values of κ given in Table I. in the previous paper referred to above. From this investigation it is evident that the coefficient λ' as usually determined is not an accurate coefficient of absorption of the total radiation passing through a plate of the substance under examination; this coefficient is the quantity λ, and $\lambda' = \lambda$ only when the thickness d is great; for very small values of d, λ' is greater than λ, and the difference is serious for substances for which κ is large. For example, when C is calculated for lead, it is found that the maximum value of λ' is $1\cdot 64\lambda$.

The method employed in this paper consists in calculating λ from suitably observed values of λ', employing the previously determined values of κ. We have then an accurate coefficient of absorption (λ) of the total radiation, primary and secondary, passing through the substance. We can then, if desired, calculate the *true* coefficient of absorption (μ) of a definite set of particles by using the relation

$$\lambda = \mu\sqrt{1 - \kappa}.$$

This *true* coefficient is, as stated above, what the coefficient of absorption would be if there were no secondary radiation.

Method of Experiment.

A lead screen *LL* is so arranged as to give a well-defined pencil of β rays coming from the radium *R*. Although not shown in the diagram, the opening in the screen is arranged so that the issuing pencil of rays consists largely of primary β rays, and not of secondary rays from the edges and sides of the aperture. *T* is an ionisation vessel of the usual type, consisting of an

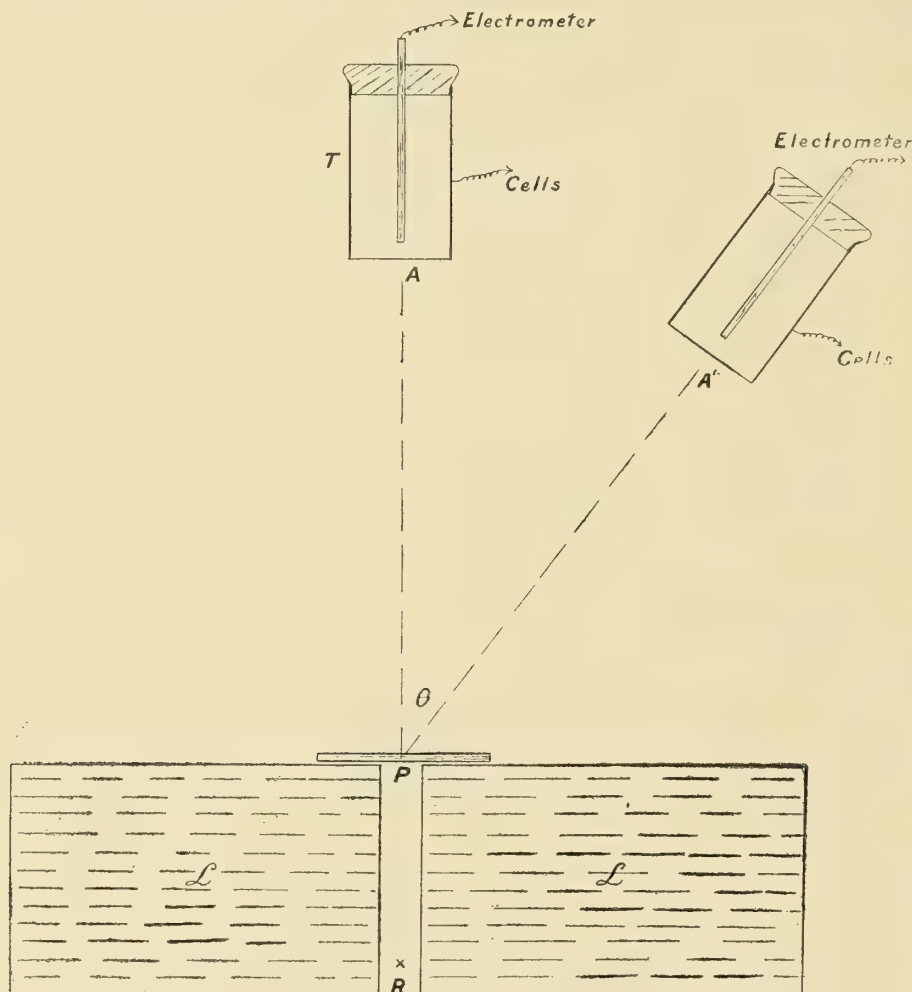
Fig. 1.

outer brass tube joined to small storage cells and with an insulated brass rod along the axis of the tube joined to an electrometer the rate of charge of which measures the ionisation produced by the rays. Plates of the substance under examination are placed at *P*, and observations are made with different thicknesses of each substance so as to be able to calculate λ from the observed

values of λ′ as explained above. In measuring the energy of the radiation passing through any given plate, observations are taken with the ionisation vessel in the position (I) represented in the diagram and also in a number of positions defined by different values of θ, the distance from the vessel to P being constant.

The apparatus is so mounted that the vessel T can readily be moved into these different positions. It is necessary to thus measure the radiation in different directions, because even when the incident pencil is chiefly in one definite direction, the portion of the issuing pencil that is composed of secondary rays has components in all directions. Even when there is no plate at P, it is necessary to take observations in different directions to get an accurate value of the energy of the incident pencil on account of the secondary rays from the walls of the opening through the lead screen.

Having taken readings for the ionisation for a number of different values of θ, a curve is plotted having for coordinates θ and the product of the reading by $\sin\theta$. The area between the curve and the axis of θ is then proportional to the total radiation leaving the plate P. This follows since the area of the portion of the hemisphere between the cones of semi-vertical angles θ and $\theta + d\theta$ is proportional to $\sin\theta\, d\theta$. Curves are plotted in this way corresponding to different thicknesses of plate P, and the areas between the curves and the axis of θ are taken as proportional to the total radiation that has passed through the plate. A value of λ′ is then calculated from this total radiation with no plate at P, and the total radiation corresponding to each thickness of plate; λ′ is, of course, calculated from the equation above

$$R_d = R_0 e^{-\lambda' d}.$$

Having thus obtained several values of λ′, we calculate the corresponding values of λ by using the equation (3) above, or rather another form of this equation more convenient for calculation. This coefficient λ is an accurate coefficient of absorption for all the radiation of primary and secondary β particles passing through the substance under examination.

Finally, when desired, we can calculate the coefficient μ from the equation

$$\lambda = \mu\sqrt{1 - \kappa}.$$

This coefficient μ, as stated above, is the true coefficient of absorption of any given set of β particles; it is what the coefficient of absorption would be if there were no secondary β radiation. In all these calculations the values of κ for the various substances are taken from the previous paper referred to above.

Second Method.

A second method of determining the coefficient λ was employed in a few experiments, and it is convenient to describe this method here before entering on an account of experimental results.

It is possible to determine λ by observations of the secondary radiations from the plate on the side on which the primary rays are incident. The coefficient of absorption is thus determined without any measurements being made of the radiations that have actually passed through the plate.

Taking the equations above:

$$R = Ae^{-x\sqrt{a^2-b^2}} + A'e^{x\sqrt{a^2-b^2}},$$

$$r = Be^{-x\sqrt{a^2-b^2}} + B'e^{x\sqrt{a^2-b^2}},$$

or

$$R = Ae^{-\lambda x} + A'e^{\lambda x},$$

$$r = Be^{-\lambda x} + B'e^{\lambda x},$$

and

$$\frac{dr}{dx} = ar - bR.$$

Using first a plate of thickness d, where d is small so that the radiation is not all absorbed, we have

$$r = 0 \quad \text{when} \quad x = d;$$

$$\therefore \quad Be^{-\lambda d} + B'e^{\lambda d} = 0. \quad (4)$$

And from the equation

$$\frac{dr}{dx} = ar - bR,$$

when $x = 0$, we have

$$(\lambda + a)B - (\lambda - a)B' = bR_0, \quad (5)$$

where R_0 is the incident radiation.

From (4) and (5) we get

$$B + B' = bR_0 \frac{e^{2\lambda d} - 1}{(\lambda + a)e^{2\lambda d} + (\lambda - a)}$$

Now, denoting by $(r_0)_d$ the secondary radiation from the plate of thickness d on the same side as the incident radiation R_0, we evidently have

$$(r_0)_d = B + B' = bR_0 \frac{e^{2\lambda d} - 1}{(\lambda + a)e^{2\lambda d} + (\lambda - a)},$$

and denoting by $(r_0)_\infty$ the similar radiation when the plate is thick enough to absorb all radiation, we have

$$(r_0)_\sigma = bR_0 \cdot \frac{1}{\lambda + a};$$

$$\therefore \quad \frac{(r_0)_\infty}{(r_0)_d} = \frac{e^{2\lambda d} + \dfrac{\lambda - a}{\lambda + a}}{e^{2\lambda d} - 1},$$

or

$$\frac{(r_0)_d}{(r_0)_\infty - (r_0)_d} = \frac{e^{2\lambda d} - 1}{\dfrac{2\lambda}{\lambda + a}},$$

or

$$e^{2\lambda d} = 1 + \frac{2\sqrt{1 - \kappa}}{\sqrt{1 - \kappa} + \left(1 - \dfrac{\kappa}{2}\right)} \cdot \frac{(r_0)_d}{(r_0)_\infty - (r_0)_d},$$

$$= 1 + \frac{1}{C} \cdot \frac{(r_0)_d}{(r_0)_\infty - (r_0)_d},$$

where C depends only on κ, and, as stated earlier in the paper where the same quantity occurred, is calculated from the values of κ for different substances given in the previous paper above referred to.

We have, therefore, the coefficient λ by measuring the secondary radiation emitted from the face on which the primary radiation falls for a plate of small thickness d, and for a plate thick enough to stop all the radiation.

It may be mentioned at once that the values of λ found by these two very different methods agree fairly well, which is of importance, not merely as regards the coefficient itself, but as affording a severe test of the general accuracy of the theoretical treatment of secondary radiation given in this and in previous papers. Practically the same theoretical work was depended upon in calculating the relative energy of the secondary rays and in making several other deductions, and it is of some importance to confirm the accuracy of the work in the way described above.

Results of Experiments.

It would occupy too much space if we gave details of all the observations. We give the numbers in some detail in the case of one of the substances examined, and the collected results are shown in a table.

Observations are first taken with no covering at P (fig. 1.), so as to obtain the intensity of the incident rays. Although not shown in the figure, the opening in the lead screen is so formed as to make the issuing pencil of β rays as cylindrical as possible, and to avoid strong secondary radiation from the lead near the place of emission. But even with such an opening there is some radiation in directions corresponding to large values of θ. Of course the radiation in these directions is of much greater relative value when a plate of the substance under examination is placed over the opening at P.

With no covering the radiation for different values of θ is given in the following table in the column headed R, and the other column gives the product of R and the corresponding value of $\sin \theta$. The actual observations are reduced to the standard of 1000 for $\theta = 0$. It should be mentioned that all through the paper the small effect produced by γ rays is corrected, so that β rays only are considered :—

θ.	R.	$R \sin \theta$.
0°	1000	—
5°	903	78·7
10°	800	139·0
15°	501	129·6
20°	314	107·4
30°	111	55·5
45°	23	16·3
60°	7	6·06
75°	—	—

Curve 1 in fig. 2. is plotted from the values of $R \sin \theta$, and the area enclosed is found to be 140·5 on the scale employed throughout. This relative value 140·5 for the energy of the incident radiation is used throughout, care being taken to reduce all observations to the same standard.

A plate of zinc, of known thickness ·00786 cms., is now placed over the opening at P, and a similar set of observations taken ; and also with a thicker

plate of ·0159 cms. The following table gives the observations on same scale as before :—

θ.	Zinc. ·00786 cms. thick.		Zinc. ·0159 cms. thick.	
	R.	R sin θ.	R.	R sin θ.
0°	204	—	115	—
15°	150	38·9	83·7	21·7
30°	85	42·5	63	31·5
45°	48	34·0	32·2	22·8
60°	23	19·8	16·6	14·4
75°	8·6	8·3	8·3	8·0

Curves 2 and 3 in fig. 2 are plotted from the values of $R \sin \theta$, and the areas enclosed are found to be 89 and 60 respectively.
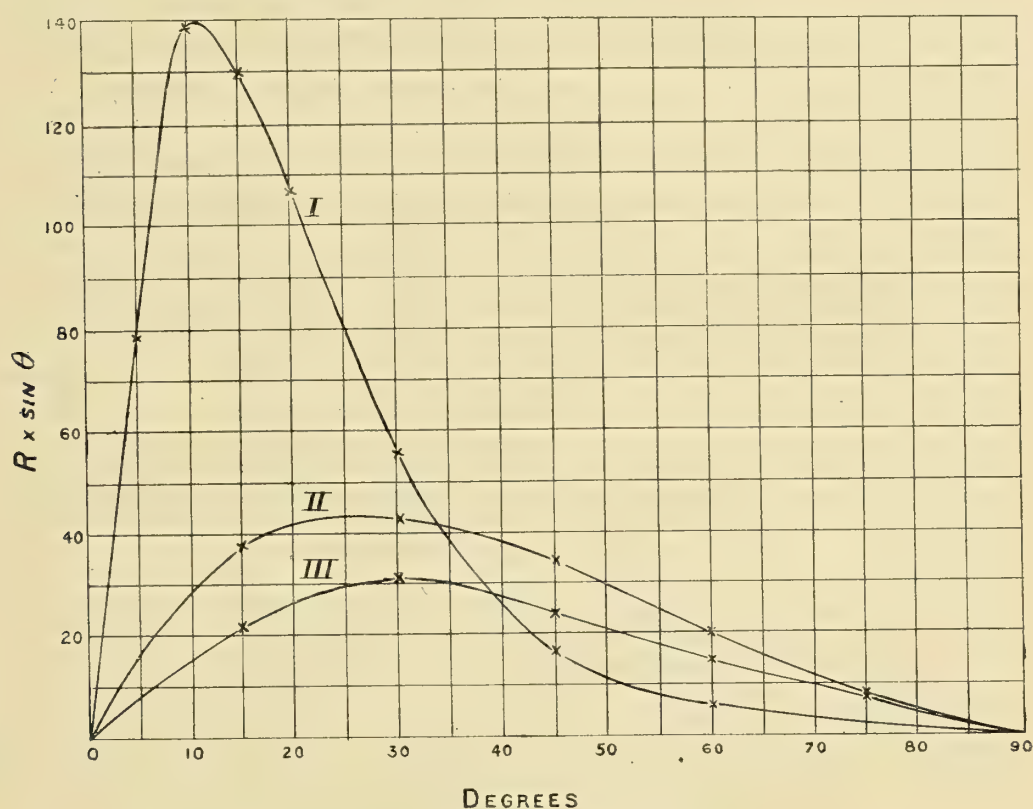

Fig. 2.

For an incident radiation of 140·5 we have, therefore, a transmission of 89 in the case of the thin zinc plate, and of 60 in the case of the thicker zinc. When

we calculate the coefficient λ' from the equation

$$R_d = R_0 e^{-\lambda' d},$$

we get the values 58 and 53·5 respectively for the two plates.   Calculating the coefficient λ as explained above (equation 3), we get the values 48 and 47 respectively.   [It is important to notice how different the values of λ' would have been had we merely taken the readings in the position $\theta = 0$, as is usually done. Instead of the ratios 140·5 : 89 and 140·5 : 60 for the intensity before and after passing through the plates, we would have had the ratios 1000 : 204 and 1000 : 115.] The values for λ obtained from plates of different thicknesses are therefore in closer agreement than the values of λ'.   Had we used thinner plates, the difference between the values of λ' would have been much greater, and even the corrected values λ would have differed considerably.   Our correction (equation 3) removes the influence of secondary radiation effects, or rather their relative effects when plates of different thicknesses are used, but does not, of course, take into account the want of homogeneity in the radiation itself.   The correction from λ' to λ is, however, of great importance, especially in the case of substances of high atomic weight for which the quantity κ (involved in equation 3) is large.

We shall now give the results of the second method described above in the case of zinc.   When using this method, observations were not made for different values of θ, and the total "reflected" radiation calculated as in the first method dealing with "transmitted" radiation.   Measurements were made at one definite angle—usually 60°—for a thin plate, and for a plate thick enough to stop all the rays, and the coefficient λ was thus obtained as described above. It would, no doubt, have been more accurate to take the measurements for various values of θ, as in the first method; but the work is laborious, and the error introduced by the shorter method is probably not very great.

The following numbers were obtained with zinc plates; the numbers are expressed in an arbitrary scale, but only ratios are used in the calculation :—

Thickness of Zinc.	Radiation.
·00786 cm.	145
·0159 cm.	199
A thick plate.	238

The first and third numbers give for λ the value 54·6, and the second and third the value 54·2.   The agreement between the values of λ obtained by the two methods is not very good in the case of zinc; it is much better in the case of some other substances, as the table below shows.   However, considering the different character of the two methods, the agreement, even in the case of zinc, is quite satisfactory, and proves the accuracy of the theoretical treatment of the subject.

The following table gives a summary of the results. As described in the case of zinc, the coefficient λ' was determined from plates of various thicknesses for each substance and λ calculated; the value given in the first column of the table is practically a mean of such determinations, special importance being attached to what were considered the more accurate observations. The second column shows the value of λ as determined by the second method; the agreement is good except in the case of copper, and the explanation of the difference in this case has not been noticed. In the succeeding columns the values of λ given in the first column have been used :—

Substance.	λ First Method.	λ Second Method.	$\dfrac{\lambda}{\text{Density}}$.	$\mu = \dfrac{\lambda}{\sqrt{1-\kappa}}$.	$\dfrac{\mu}{\text{Density}}$.	Atomic Weight.
Lead, . .	91	95	8·0	268	23·4	206·4
Platinum, .	173	174	8·0	479	22·3	194·3
Tin, . .	54	50	7·4	133	18·2	118·8
Cadmium, .	66	65	7·5	160	18·6	112·0
Silver, . .	85	83	8·0	203	19·1	108·0
Zinc, . .	48	54	6·6	103	14·3	65·4
Copper, . .	50	61	5·6	107	12·0	63·2
Nickel, . .	63	63	7·6	127	15·3	59·0
Aluminium, .	14	—	5·0	23	8·5	27·0

Discussion of Results.

The ratio of the coefficient λ to the density varies very considerably, and, what is more important, the variation is irregular. We learn little, therefore, as to the stopping power of different types of atoms by measuring this coefficient λ for equal weight thicknesses of different forms of matter. When we turn to the coefficient μ, the manner of its variation is at once apparent. It will be remembered that μ is what the coefficient of absorption would be if there were no secondary β rays; it is the *true* coefficient of absorption of any given set of particles. As shown above,

$$\mu = \frac{\lambda}{\sqrt{1-\kappa}},$$

where κ is the ratio of the energy of the secondary particles emitted from an element of volume to that of the particles absorbed in that element. The values of κ are taken from the previous paper. The column in the table giving the

ratio of μ to the density shows quite clearly that, on the whole, this ratio increases with the atomic weight.   Further, the elements fall into divisions with respect to this ratio, the divisions being the same as the chemical *periods*.   Thus, lead and platinum are in one period; tin, cadmium, and silver in another; zinc, copper, and nickel in a third ; and aluminium in a fourth.   It would be useful to examine more elements ; but the above are sufficient to show the dependence on atomic weight of the coefficient μ for plates of different elements of equal weight per unit area.   The numbers given also show clearly enough the divisions corresponding to the chemical *periods* ; but more determinations would be necessary to show how the coefficient varies from one element to another in the same period.   That the atomic weight should be the factor that determines the absorption produced by equal weight thicknesses of different elements is quite intelligible.   The actual stoppage of a β particle is, no doubt, brought about by electric force and not by mere mechanical impact.   If, then, a main distinction between different atoms consists in a difference of number and grouping of electrons, the stopping power per atom should increase more rapidly than the number of electrons, or than the atomic weight, so that few atoms of high atomic weight should be more effective than an equal mass of atoms of smaller atomic weight.

Crowther[*] has recently determined the coefficient of absorption λ of the β rays of uranium for a large number of substances.   The present paper shows how necessary it is to distinguish between λ and the true coefficient μ when the secondary radiation is great, as it is for β radium rays ; but in the case of β uranium rays Crowther finds the secondary radiation so small that he considers the distinction between λ and μ becomes unimportant.

Our results as regards the general connexion between the atomic weight and the ratio of μ to the density are in agreement with Crowther's ; and his results also show the nature of the variation of the ratio of λ to density between elements in the same period.

The comparative unimportance of secondary radiation effects in the case of β uranium rays, as found by Crowther, is striking when compared with these effects in the case of β rays from radium, and is a point that requires investigation.

[*] Phil. Mag., Oct. 1906.

TRANSACTIONS (SERIES II.).

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VOLUME IX.—(SERIES II.)

V.

ELECTRO-MAGNETIC MASS.

BY

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CONTENTS.

I.—INTRODUCTION.

In the formation of a rational scheme of electrodynamics two groups of assumptions are necessary. In the first place, principles must be laid down for deducing the values of the electric and magnetic forces in terms of the distribution and motion of the electrons. In the Maxwellian scheme this is effected by the circuital relations, or by what is equivalent to them, certain direct assumptions as to the values of the electro-magnetic vectors.* In the second place, hypotheses must be proposed which will determine the motion of various distributions of electrons in terms of the field of force in which they are situated. This involves expressions for energy, energy flux, momentum coefficients of self-induction, mass, etc. It is the object of the present paper to deduce all these expressions from a single principle—the inequality of action and reaction. Starting with any assigned system of electrical matter moving in a general manner, the values of the electrical and magnetic forces become completely definite. The electromotive forces experienced by any portion of this system consist of two parts—one arising from other parts of

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* Trans. Roy. Dublin Soc., vol. viii., part iii.

the same system, the other arising from external sources. Then the principle we proposed to use is that *the internal forces when treated according to the ordinary laws of statics will amount to a force and couple equal and opposite to that due to external sources.* Conceiving an electron to be a rigid electrical system, we reproduce the properties of Newtonian mass; whilst from more general systems we arrive at the conventional expressions for induction coefficients, energy, and energy flux, momentum, linear and angular, and the stresses of Maxwell.

II.—The Circuital Relations.

The electric force $(X,\ Y,\ Z)$ and the magnetic force $(\alpha,\ \beta,\ \gamma)$ are connected by the circuital relations in free æther

$$V^{-2}\partial/\partial t\,(X,\ Y,\ Z) = \mathrm{Curl}\,(\alpha,\ \beta,\ \gamma)$$

$$-\,\partial/\partial t\,(\alpha,\ \beta,\ \gamma) = \mathrm{Curl}\,(X,\ Y,\ Z).$$

These equations involve the facts that $\partial X/\partial x + \partial Y/\partial y + \partial Z/\partial z$, and $\partial\alpha/\partial x + \partial\beta/\partial y + \partial\gamma/\partial z$, are independent of the time. In the scheme of Maxwell, we take these expressions to be zero.

If the electricity has a volume-distribution ρ, the above equations have to be modified. The vector sum of the products of each charge in a volume element by its velocity is a certain vector $(i_1,\ i_2,\ i_3)\,d\tau$, where $d\tau$ is the volume element. The fact of the persistence of electric charge gives rise to the equation of continuity

$$\partial\rho/\partial t + \partial i_1/\partial x + \partial i_2/\partial y + \partial i_3/\partial z = 0.$$

The modified equations are

$$V^{-2}\partial/\partial t\,(X,\ Y\ Z) + 4\pi\,(i_1,\ i_2,\ i_3) = \mathrm{Curl}\,(\alpha,\ \beta,\ \gamma),$$

$$-\,\partial/\partial t\,(\alpha,\ \beta,\ \gamma) = \mathrm{Curl}\,(X,\ Y,\ Z).$$

As before,

$$\partial\alpha/\partial x + \partial\beta/\partial y + \partial\gamma/\partial z = 0\ ;$$

but

$$\partial X/\partial x + \partial Y/\partial y + \partial Z/\partial z = 4\pi\rho\,V^2.$$

If the distribution of electricity is a surface-distribution, which in the most general case we may take to be in motion, we have the following boundary conditions.* Take the Z-axis normal to the surface, so that the plane of xy is the tangent plane, and let the values of the vectors on the positive side of the

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* Trans. Roy. Dublin Soc., vol. viii., part vii.

tangent plane be denoted by the single accent, and on the negative side by the double accent, and let w be the normal velocity of the surface, then :—

$$- w V^{-2} (X' - X'') + 4\pi i_1 = - (\beta' - \beta''),$$

$$- \dot{w} V^{-2} (Y' - Y'') + 4\pi i_2 = \alpha' - \alpha'',$$

$$- w V^{-2} (Z' - Z'') + 4\pi i_3 = 0,$$

$$w (\alpha' - \alpha'') = - (Y' - Y''),$$

$$w (\beta' - \beta'') = X' - X'',$$

$$\gamma' - \gamma'' = 0.$$

III.—The Fundamental Assumption.

In dynamics we pass from the case of a particle to that of a rigid body by means of D'Alembert's principle.

This principle, by asserting that the internal reactions of such a body are in equilibrium amongst themselves, enables us to dispense with such reactions in our equations. The assumption which we are going to make use of here is of a similar nature, and is as follows :—*The internal electro-magnetic forces of an electrical system are in equilibrium with the external electro-magnetic forces.*

IV.—Deductions of Expressions for Momentum and Energy.

Let us consider an electrical system of density ρ, the current vector being (i_1, i_2, i_3), and let the forces arising from this be (X, Y, Z) and (α, β, γ), the external field of force in which the system is situated being denoted by (X_0, Y_0, Z_0) $(\alpha_0, \beta_0, \gamma_0)$. The internal force along the x-axis acting on the element $d\tau$ is $(X\rho + \gamma i_2 - \beta i_3), d\tau$; and the external force is $X_0\rho + \gamma_0 i_2 - \beta_0 i_3$. As a first example let us consider the activity of the forces. Taken collectively they are in equilibrium ; hence the total activity is zero, or the reversed activity of the internal forces is the rate at which energy is supplied from outside, *i.e.*, the former expression gives us the rate of change of the electro-magnetic energy of the system. The reversed activity is obviously

$$- \iiint d\tau (X i_1 + Y i_2 + Z i_3).$$

Substituting for $(i_1, \dot{i_2}, i_3)$ from the circuital relations, we find that the subject of integration becomes

$$(8\pi)^{-1} V^{-2} \partial/\partial t (X^2 + Y^2 + Z^2) + (8\pi)^{-1} \partial/\partial t (\alpha^2 + \beta^2 + \gamma^2)$$

$$- (4\pi)^{-1} \{ \partial/\partial x [\beta Z - \gamma Y] + \partial/\partial y (\gamma X - \alpha Z) + \partial/\partial z (\alpha Y - \beta X) \}.$$

L 2

We can infer from this that the energy per unit of volume is represented by

$$(8\pi)^{-1}\{ V^{-2}(X^2 + Y^2 + Z^2) + \alpha^2 + \beta^2 + \gamma^2)\},$$

which is Maxwell's expression, and that the energy-flux is $(4\pi)^{-1}$, the vector product of the magnetic into the electric force, which is the Poynting flux.

By similar reasoning the resolved part of the reversed internal forces must represent the rate of change of momentum of the system. We have in this case to evaluate

$$- \iiint d\tau \left[X\rho + \gamma i_2 - \beta i_3 \right].$$

After some reduction we obtain for the subject of integration

$$(8\pi)^{-1} V^{-2}\{ - \partial/\partial x \,(X^2 - Y^2 - Z^2) - \partial/\partial y \,(2XY) - \partial/\partial z \,(2XZ)\},$$
$$+ (8\pi)^{-1}\{ - \partial/\partial x \,(\alpha^2 - \beta^2 - \gamma^2) - \partial/\partial y \,(2\alpha\beta) - \partial/\partial z \,(2\alpha\gamma)\},$$
$$+ (4\pi)^{-1} V^{-2}\partial/\partial t \,(\gamma Y - \beta Z).$$

The interpretation of these expressions gives us the electric and magnetic stresses of Maxwell, and the fact that the linear momentum per unit volume is $(4\pi)^{-1} V^{-2}$, the vector product of the electric into the magnetic force.

By taking moments about any line we arrive in a similar manner at an expression for the angular momentum; and it is the moment of the expression for the momentum written above.

A difficulty arises in the analytical working out of the above results when a surface-distribution occurs. As an example of the method of proceeding, we shall consider only one case, that of the equation of activity.

The rate of change of energy of the system is the surface integral of the scalar product (in Hamilton's sense) of the electric force and the current.

The electric force is now the arithmetical mean between the values on each side of the surface, so that, using the same axes as in the boundary conditions of § 2, an element of the integral is

$$- \tfrac{1}{2}(X' + X'')\,i_1 - \tfrac{1}{2}(Y' + Y'')\,i_2 - \tfrac{1}{2}(Z' + Z'')\,i_3,$$

which becomes, on replacing $(i_1 i_2 i_3)$ by its value in terms of the forces,

$$- w\,(8\pi)^{-1} V^{-2}(X'^2 + Y'^2 + Z'^2 - X''^2 - Y''^2 - Z''^2)$$
$$+ (8\pi)^{-1}(\beta' - \beta'')(X' + X'') - (8\pi)^{-1}(\alpha' - \alpha'')(Y' + Y'');$$

add to this

$$(8\pi)^{-1}(\beta' + \beta'')(X' - X'') - (8\pi)^{-1}(\alpha' + \alpha'')(Y' - Y'')$$
$$- w\,(8\pi)^{-1}(\alpha'^2 + \beta'^2 - \alpha''^2 - \beta''^2),$$

which is zero ; and we get

$$- w \, (8\pi)^{-1} V^{-2}(X'^2 + Y'^2 + Z'^2 - X''^2 - Y''^2 - Z''^2)$$
$$- w \, (8\pi)^{-1} V^{-2}(a'^2 + \beta'^2 - a''^2 - \beta''^2) + (4\pi)^{-1}(\beta' X' - a' Y')$$
$$- (4\pi)^{-1}(\beta'' X'' - a'' Y'') \, ;$$

or if T', T''' denote the values just outside and just inside the surface of the expression which we called before the electro-magnetic energy, and N', N'', the values of the Poynting vector resolved along the normal, the expression for the activity becomes $- \iint w \, (T'' - T''') \, dS - \iint (N' - N'') \, dS.$

Suppose, in order to fix our ideas, that the moving surface is closed and contained with a fixed surface, the element of which we denote by $d\Sigma$, there being no electricity inside Σ except on S. We have then to prove that the above expression is identical with

$$\iint N d\Sigma + d/dt \iiint T' d\tau' + d/dt \iiint T'' d\tau'',$$

where the second integral refers to the space inside Σ, and outside S, and the third integral to the space within S.

We have in fact

$$d/dt \iiint T' d\tau' = \iiint \partial T'/\partial t \; d\tau' - \iint w T' dS = \iint N d\Sigma - \iint N' dS - \iint w T' dS,$$

and

$$d/dt \iiint T'' d\tau'' = \iint N'' dS + \iint w T'' dS,$$

so that the result follows at once.

V.—The Retarded Potential.

The electric force can be expressed in form

$$V^{-2}(X, \, Y, \, Z) = - \, (\partial/\partial x, \, \partial/\partial y, \, \partial/\partial z)\psi - \partial/\partial t(F, \, G, \, H),$$

and the magnetic force is given by

$$(a, \, \beta, \, \gamma) = \mathrm{Curl} \, (F, \, G, \, H),$$

where ψ is the scalar potential, and $(F, \, G, \, H)$ is the vector potential. In the case of a single electron the solutions are given by the retarded potential.[*] For slow motions it will be found convenient to express the retarded potential in terms of the distance, not at the retarded time, but at the actual time; and in doing this, we can at the same time expand in inverse powers of V.

[*] Cf. Proc. London Mathematical Soc., ser. 2., vol. i.

If r denotes the distance of the electron e at the time t from the point (x, y, z), we can easily verify from the equation

$$\nabla^2 \psi = V^{-2} \partial^2 \phi / \partial t^2,$$

that

$$\psi = e \left\{ \frac{1}{r} + \frac{1}{2!\,V^2} \frac{\partial^2 r}{\partial t^2} + \frac{1}{4!\,V^4} \frac{\partial^4 r^3}{\partial t^4} + \cdots \right\},$$

or to the second power of $\dfrac{1}{V}$

$$\psi = e \left[\frac{1}{r} + \frac{1}{2!\,V^2} \frac{\partial^2 r}{\partial t^2} \right].$$

To the same approximation

$$(F,\ G,\ H) = e \, \frac{\dot{x}_1,\ \dot{y}_1,\ \dot{z}_1)}{V^2 r},$$

where $(\dot{x}_1, \dot{y}_1, \dot{z}_1)$ is the velocity of the electron. When there is a great number of electrons moving over small paths, it is more convenient to refer to fixed volume elements.[*] In this case the scalar potential due to a volume element $d\tau$ is $\rho\, d\tau / r$, where ρ is the density at the time $t - r/V$, whilst the vector potential is $(i_1, i_2, i_3)\, d\tau / V^2 r$, where (i_1, i_2, i_3) denotes the current.

In the first case let us consider the mutual forces of two portions of electricity A and B moving with the same velocity. On rejecting the parts of the mutual forces which balance, we have left only a scalar potential

$$- \left(\ddot{x}_1 \frac{\partial r}{\partial x} + \ddot{y}_1 \frac{\partial r}{\partial y} + \ddot{z}_1 \frac{\partial r}{\partial z} \right),$$

and from the vector potential we get components of force

$$- e \, (\ddot{x}_1,\ \ddot{y}_1,\ \ddot{z}_1) / r.$$

We thus get for the electric force two parts: the one opposite in direction to the acceleration f and equal to ef/r, and the other at right angles to the line joining A to B and equal to $ef \cos \phi / r$, where ϕ is the angle which AB makes with the acceleration.

In the second case if, as in the case of conduction currents, the electrical density is zero, the only portion of the force to be considered is ef/r.

[*] Proc. London Mathematical Soc., *loc. cit.*

VI.—THE COEFFICIENTS OF INDUCTION.

As an example of the methods of the preceding Article, let us consider the action of a moving electron on a fixed, closed, conducting circuit.

The activity communicated to the circuit will be the line integral of the product of the electric force resolved along the curve and the current at each point. The current being of constant magnitude will appear as a factor in the result; the other factor will be the "electromotive force" due to the motion. It becomes at once clear that we are to reject the parts of the electric force which arise from the scalar potential, so that the electromotive force is

$$V^2 \int \left(\frac{\partial F}{\partial t} \, dx + \frac{\partial G}{\partial t} \, dy + \frac{\partial H}{\partial t} \, dz \right) = e \frac{\partial}{\partial t} \int (\dot{x}_1 dx + \dot{y}_1 dy + \dot{z}_1 dz)$$

$$\times \left\{ r_1 - \left[(x - x_1) \dot{x}_1 + (y - y_1) \dot{y}_1 + (z - z_1) \dot{z}_1 \right] V^{-1} \right\};$$

when the speed is slow, this becomes

$$\frac{\partial}{\partial t} \int e \left(\dot{x}_1 dx + \dot{y}_1 dy + \dot{z}_1 dz \right) / r.$$

If the moving electron forms part of a current, we evidently reproduce the ordinary expression for the electromotive force of induction.

VII.—NEWTONIAN MASS.

Consider first the case of an electric system moving with uniform velocity in a straight line. Let P_1 and P_2 be any two points of the system at the time t, then it follows from the results of S that the electric force of P_1 and P_2 is equal and opposite to that of P_2 on P_1, so that the activity of the internal forces is zero, and the system, if symmetrical about the direction of motion, will continue its motion. This represents the Newtonian law of inertia.

The system will not, however, be in relative equilibrium in general. For the system of internal reactions will be in general equivalent to a couple. In a similar manner we can treat of the slow motion of any system. We shall confine ourselves to the following problem. A system moves with a motion of translation: what is the resultant of the internal reactions? For brevity, we shall put our results in the quaternion form. Let the vectors to the various charges $e_1, e_2, \ldots$ be denoted by $\rho_1, \rho_2, \ldots$. The force exerted by any charge e_r at the extremity of the vector ρ is equal to

$$e_r V (\rho - \rho_r) V \sigma (\rho - \rho_r) \left[T (\rho - \rho_r) \right]^{-3},$$

where σ is the acceleration.

Hence the resultant force is given by

$$\tfrac{1}{2}\,\Sigma\Sigma e_r e_s\, V(\rho_s - \rho_r)\, V\sigma(\rho_s - \rho_r)\,[T(\rho_s - \rho_r)]^{-3},$$

or as we may write it $\phi(\sigma)$, where ϕ is a linear self-conjugate vector function. This suggests at once the following theorems. There exists a quadric

$$S\sigma\phi\sigma = \text{const.},$$

such that if the acceleration takes place along the radius vector, the opposing force will have its direction normal to the quadric at the extremity of the radius vector and inversely proportional to the length of the perpendicular from the centre on the tangent plane. In general, there will be only three directions, for which the direction of the opposing force will coincide with the direction of the acceleration.

If we define the "mass" in any direction to be the resolved part of the opposing force along the unit acceleration in that direction, we see that the mass in any direction is inversely proportional to the square of the corresponding radius vector of the quadric $S\sigma\phi\sigma = \text{const.}$ in that direction. This quadric might be called the *mass-quadric*. Of actual importance, perhaps, would be the mean value of the mass, *i.e.*, the mean value of the vector function

$$\tfrac{1}{2}\,\Sigma\Sigma e_r e_s\, V(\rho_r - \rho_s)\, V\sigma(\rho_r - \rho_s)\,[T(\rho_r - \rho_s)]^{-3},$$

in which every direction of σ with reference to the system is equally probable.

Expanding, we get

$$\tfrac{1}{2}\,\Sigma\Sigma e_r e_s\,[\sigma(\rho_r - \rho_s)^2 - (\rho_r - \rho_s)\,S\sigma(\rho_r - \rho_s)]\,[T(\rho_r - \rho_s)]^{\frac{3}{2}}.$$

For the mass in any direction $U\sigma$ we get

$$-\tfrac{1}{2}\,\Sigma\Sigma e_r e_s\,[-(\rho_r - \rho_s)^2 - [S U\sigma(\rho_r - \rho_s)]^2]\,[T(\rho_r - \rho_s)]^2.$$

The mean value of $[S U\sigma(\rho_r - \rho_s)]^2$ is evidently

$$-\tfrac{1}{3}(\rho_r - \rho_s)^2.$$

Hence the mean mass is

$$\tfrac{2}{3}\,\Sigma\Sigma e_r e_s\,[T(\rho_r - \rho_s)]^{-1},$$

or, as we may put it, $\tfrac{4}{3}V^{-2}$, the work done in assembling tne system from a state of infinite diffusion.

TRANSACTIONS (SERIES II.).

VOLUME IX.

THE

SCIENTIFIC TRANSACTIONS

OF THE

ROYAL DUBLIN SOCIETY.

VOLUME IX.—(SERIES II.)

VI.

THE DENSITIES AND SPECIFIC HEATS OF SOME ALLOYS OF IRON.

BY

W. BROWN, B.Sc.

VI.
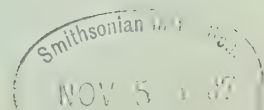
THE DENSITIES AND SPECIFIC HEATS OF SOME ALLOYS OF IRON.

By W. BROWN, B.Sc.

[Read, June 18, 1907.]

INTRODUCTION.

THE electric and magnetic properties of an extensive series of steels or alloys of iron were investigated in the Physical Laboratory of the Royal College of Science, Dublin, from 1895 to 1903; and the results were published at intervals in the Scientific Transactions of the Royal Dublin Society.* The alloys were all made at the Hecla Steel Works, Sheffield, and their chemical composition was determined in the Chemical Laboratory attached to the Hecla Works.

For some time past the present writer has been investigating the thermal capacity of these various alloys, and has measured the densities and specific heats of about forty different samples; and the work done forms the subject of this communication. The specimens were all carefully prepared and cleaned for these experiments; and to make sure that they would all be in the same physical state, they were raised to a bright red heat in a furnace, and dropped into water at about 16° C., then finally cleaned up, and polished with fine emery.

In the chemical composition given in the following tables, it is assumed that in all cases *iron* makes up the total to 100.

PART I.—DENSITY.

For the determination of the densities of the specimens, a small specific-gravity bottle was specially made for the purpose. It is about 3 cm. long and 1 cm. in diameter, with perforated stopper, and has a flange on the bottom, so as to enable

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* Barrett, Brown, and Hadfield, Scient. Trans. Roy. Dublin Soc., 1900, 1902, 1904.

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it to stand vertically on the scale-pan of a chemical balance. The measurements were all made between the temperatures of 12° and 16° C.

In order to find the density of the water used in each experiment, a curve was plotted on a large scale indicating the temperature and density of water from the values given in the Physical Tables of Landolt and Börnstein. There was also plotted on a large scale a curve showing the temperature and weight of the specific-gravity bottle filled with distilled water; and in the work all the usual and necessary precautions were taken to avoid errors. The densities of all the specimens were determined by means of the specific-gravity bottle; but on account of the small mass of the material (3 to 4 grammes) and the difficulty of getting them quite clear of minute air-bubbles, all the measurements were repeated by the ordinary hydrostatic method. In both these sets of experiments on the density, as well as the experiments on the specific heat, a Sartorius chemical balance was employed, which weighed accurately to one-tenth of a milligrame. In order to avoid any correction for the suspending thread in the density experiments by the second method, a very fine, strong fibre of floss silk was used, which weighed only about one quarter of a milligramme per metre, and could therefore be neglected.

The values of the densities given below are each the mean of three or more different experiments, and no result was accepted that differed by more than *one* in the third decimal place.

In the following tables are tabulated:—(1) the percentage chemical composition of the alloys, with the exception of the iron present, which is understood in all cases to make up the total to 100; (2) the observed density of each specimen; (3) the reciprocal of the density or the specific volume; (4) the mean specific volume of the alloy or that calculated from the specific volumes of the constituents, assuming that neither expansion nor contraction takes place; (5) the differences between the calculated and the observed specific volumes of each sample. From the specific volume or the volume in cubic centimetres occupied by one gramme of the material, the effect of adding a foreign substance to the iron can best be seen.

Table I.

Carbon Steels.

Mark	Percentage Composition			Density	Specific Volume		
	C	Si	Mn		Observed	Calculated	Difference
S. C. I.	0·028	0·07	—	7·8771	0·12695	0·12719	0·00024
L. S. S.	0·05	0·02	0·18	7·8778	0·12694	0·12713	0·00019
1166 A	0·14	0·08	—	7·8638	0·12716	0·12756	0·00040
1392 A	0·85	0·17	0·32	7·8268	0·12777	0·13004	0·00227
1392 G	1·23	0·12	0·14	7·7897	0·12827	0·13104	0·00277
611	0·58	0·49	0·58	7·8132	0·12800	0·13016	0·00216
613	1·00	0·49	0·58	7·7587	0·12890	0·13146	0·00256
614	1·25	0·46	0·62	7·7525	0·12900	0·13214	0·00314

In Table I. are given the results for eight carbon steels which contain from 0·028 to 1·25 per cent. of carbon ; and from the two columns of specific volumes it will be seen that contraction has taken place in each case. In order to find the effect on the specific volume of the material produced by the addition of *carbon* alone to the iron, we must make a correction for the presence of the other constituents ; and from the results given in Table V., page 66, for the silicon steels, it was found that the *increase* in the specific volume of the material produced by adding *one* per cent. of silicon to iron was 0·0011 c.c.

By comparing the two specimens marked S.C.I. and 1166 A in Table I. (which have approximately the same amount of silicon), it will be found that for an increase of 0·112 per cent. of carbon to the iron, the specific volume of the material is increased by 0·00021 c.c., and therefore 1 per cent. of added carbon will increase the specific volume of the alloy at the rate of 0·0018 c.c.—a result the same as that obtained by Mr. C. Benedicks in tests on some Swedish steels.[*]

Applying this result to the specimen S.C.I., its specific volume when corrected for carbon becomes 0·1269 c.c., which may be taken as the value for practically pure iron. If on adding *one* per cent. of carbon to iron no change took place

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[*] Recherches Physiques et Physico-chimiques sur l'Acier au Carbone. Upsala, 1904.

in the specific volumes of the constituents, then the specific volume of the alloy would exceed that of pure iron by 0·00308 c.c.; and since the observed value is 0·0018 c.c., the difference, 0·00128 c.c., shows that a decided contraction has taken place.   Taking the first three specimens in Table I., and plotting as abscissæ the percentage amount of carbon present, and as ordinates the specific volumes of the material when corrected for silicon, it will be found that the points lie practically on a straight line which cuts the axis of ordinates at 0·1269, the value for pure iron; hence the effect on the specific volume of the material obtained by adding up to about 0·2 per cent. of carbon to iron may be expressed thus :—specific volume = 0·1269 + 0·0018 C, when C represents the percentage amount of carbon added.

By comparing the high carbon steels 1392 A and 1392 G, and also 611 with 614, we find that the specific volume of the material is increased by 0·0015 c.c. for every 1 per cent. of added carbon.

Table II.

Manganese Steels.

Mark	Percentage Composition		Density	Specific Volume.		Difference
	C	Mn		Observed	Calculated	
48	0·20	0·50	7·8456	0·12746	0·12756	0·00010
4147	0·24	1·00	7·8354	0·12762	0·12772	0·00010
53	0·41	2·25	7·7983	0·12823	0·12835	0·00012
39	0·36	4·00	7·8352	0·12763	0·12834	0·00071
1323 C	0·15	5·40	7·8411	0·12753	0·12781	0·00028
945 A	1·20	7·00	7·9028	0·12654	0·13118	0·00464
1338 B	0·26	13·00	7·9970	0·12505	0·12879	0·00374
598	1·54	18·50	7·9075	0·12646	0·13319	0·00673

In Table II. the results are given for eight manganese steels which have from 0·5 to 18·5 per cent. of manganese present; and from the specific volume columns it will be seen that in every case contraction takes place.

If the values of the observed specific volumes be corrected for carbon, and the results plotted in a curve with the percentage of manganese as abscissæ, and the

corrected specific volumes as ordinates, it will be found that the specific volume of the material is slightly *increased* up to about 2 per cent. of manganese added, and after that the specific volume is steadily *decreased*.

This curve will show that up to about 2 per cent. of added manganese the specific volume of the material is increased about 0·00026 for every 1 per cent. of manganese present.

The specific volume of the alloy—corrected for carbon—when 18·5 per cent. of manganese is present, is 0·1240 c.c.; and hence between the limits of 4 and 18·5 per cent. of manganese the specific volume of the material is *decreased* at the rate of about 0·00015 c.c. for every 1 per cent. of manganese added.

TABLE III.

NICKEL STEELS.

| Mark | Percentage Composition | | | | Density | Specific Volume | | |
	C	Si	Mn	Ni		Observed	Calculated	Difference
1397 B	0·26	0·33	0·18	0·58	7·8294	0·12773	0·12859	− 0·00086
1287 D	0·14	0·21	0·72	1·92	7·8675	0·12711	0·12771	− 0·00060
1287 E	0·19	0·20	0·65	3·82	7·8570	0·12727	0·12757	− 0·00030
1447 A	0·81	0·39	0·61	12·70	7·7952	0·12828	0·12874	− 0·00046
1287 K	0·19	0·27	0·93	19·64	7·8860	0·12682	0·12550	+ 0·00132
1287 L	0·16	0·30	1·00	24·51	7·9335	0·12605	0·12479	+ 0·00126
1449 A	0·70		0·82	31·40	8·0286	0·12456	0·12457	0·00000

In Table III. are given the results for seven nickel steels which contain from 0·58 to 31·4 per cent. of nickel, and from the columns of specific volume it will be observed that the addition of nickel to iron up to about 12 per cent. causes a contraction in the specific volume of the alloy; whilst at about 20 per cent. of nickel present a distinct expansion takes place, and when there is 31·4 per cent. of nickel present, the calculated specific volume is practically the same as that obtained by experiment.

In fig. 1 (page 64) are plotted the percentage amounts of nickel present as abscissæ, and as ordinates the observed values of the specific volumes, as well as the values corrected for carbon and silicon, the effect of manganese being neglected. It will be seen from the curve that the specific volume of the material is at first

slightly *decreased* and then slightly *increased* up to about 4 per cent. of nickel present, whilst the specific volume of the material is decreased very little by the further addition of about 16 per cent. of nickel.

From the curve we see that the specific volume of the material—corrected for carbon and silicon—which contains 20 per cent. of nickel, is 0·12630 c.c., and the specific volume of the constituents of the alloy, if no change had taken place, would be 0·1240 c.c., so that for this specimen we have an expansion of about 0·0023 c.c.
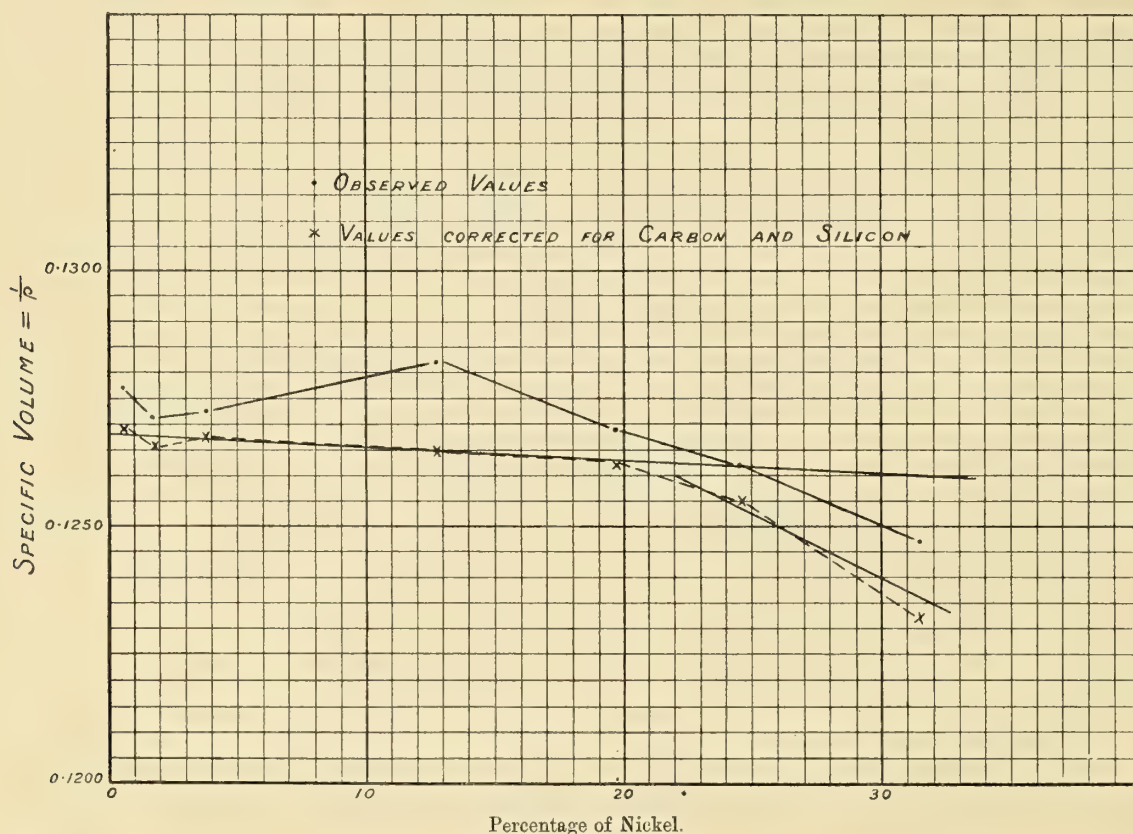
Percentage of Nickel.
Fig. 1.—Nickel Steels.

By drawing a *mean* line as in fig. 1, we find that the addition of 20 per cent. of nickel to iron decreases the specific volume of the material by 0·0006 c.c., or at the rate of about 0·00003 c.c. for every 1 per cent. of added nickel, so that up to about 20 per cent. of nickel the change in the specific volume of the material may be expressed as spec. vol. = 0.1269 − 0·00003 Ni where Ni represents the percentage of nickel present.

For the high nickel steels, if we take a mean line through the points in fig. 1 for the last three specimens, we find that the addition of 10 per cent. of nickel to an iron-nickel alloy which already contains 20 per cent. of nickel *decreases* the specific volume of the material by 0·0023 c.c., or at the rate of about 0·00023 c.c. for every 1 per cent. of nickel further added.

Table IV.

Tungsten Steels.

Mark	Percentage Composition			Density	Specific Volume		Difference
	C	Mn	W		Observed	Calculated	
1294 F	0·16	0·11	1·0	7·9365	0·12600	0·12666	0·00066
1294 H	0·28	0·28	3·5	8·0645	0·12400	0·12517	0·00117
1294 I	0·38	0·20	7·5	8·2918	0·12060	0·12249	0·00189
1294 L	0·76	0·28	15·5	8·7720	0·11400	0·11769	0·00369

In Table IV. the results for four tungsten steels are given, and they show the great effect that tungsten has on the density when alloyed with iron, and the columns of the specific volumes show that a very decided contraction has taken place in the alloys.
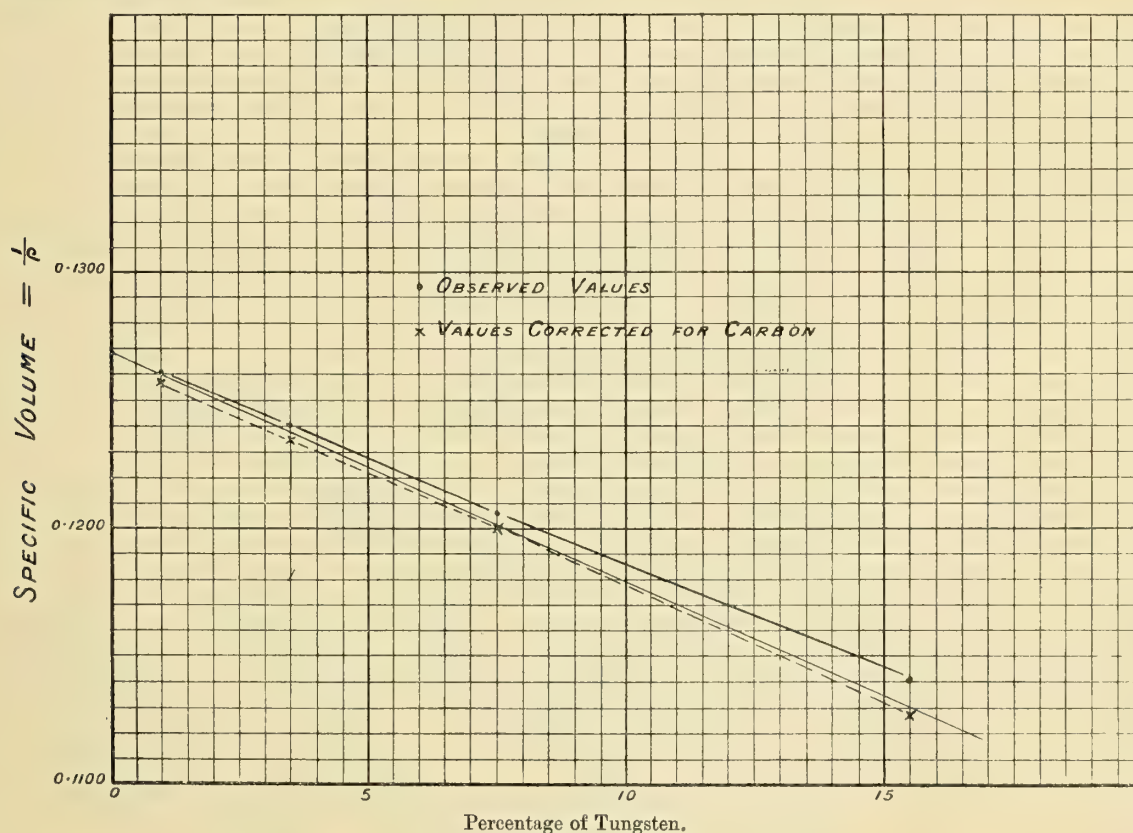
Fig. 2.—Tungsten Steels.

In fig. 2 are plotted the observed values of the specific volumes as well

as the values corrected for carbon ; and by drawing a mean line through the points for the corrected values, we see that the addition of 15·5 per cent. of tungsten to iron *decreases* the specific volume of the material by 0.0139 c.c., or at the rate of 0·0009 c.c. for every *one* per cent. of added tungsten ; and therefore the effect of adding tungsten to iron may be expressed as specific volume = 0·1269 − 0·0009 W, where W represents the percentage amount of tungsten present.

If on adding *one* per cent of tungsten to 99 per cent. of iron, no change were to take place in the specific volumes of the constituents, the resultant mean specific volume of the material would be 0.12615 c.c., which is less than that of pure iron by 0·00075 c.c. ; and the observed mean value of the change in the specific volume per *one* per cent. over a range from 0 to 15·5 per cent. of tungsten being 0·0009 c.c., a slight expansion has therefore taken place.

TABLE V.

SILICON STEELS.

Mark	Percentage Composition		Density	Specific Volume		
	C	Si		Observed	Calculated	Difference
S. C. I.	0·028	0·07	7·8771	0·12695	0·12719	0·00024
898 E.	0·20	2·50	7·6934	0·12998	0·13480	0·00482
898 H.	0·26	5·50	7·5100	0·13315	0·14373	0·01058

In Table V. are given the results obtained from two silicon steels which contain 2·5 and 5·5 per cent of silicon respectively, the result for the pure iron S.C.I. being also put here for comparison.

For the high percentage of silicon a distinct contraction has taken place in the alloy, as is evident from the column of differences in the specific volumes.

In fig. 3 are plotted the observed values of the specific volumes, as well as the values corrected for carbon ; and by drawing a mean line through the points in the corrected curve we find that an addition of 5·5 per cent. of silicon to iron *increases* the specific volume of the alloy by 0·00595 c.c., or at the rate of about 0·0011 c.c. for every *one* per cent. of added silicon, i.e., specific volume = 0·1269 + 0·0011 Si, where Si represents the percentage amount of silicon in the alloy.

If no change were to take place in the specific volumes of the constituents when 1 per cent. of silicon is added to 99 per cent. of iron, the specific volume

of the material would be greater than that of pure iron by 0·0029 c.c.; and since the observed difference is 0·0011 c.c., the difference of these two, 0·0018 c.c., shows that a decided contraction has taken place.
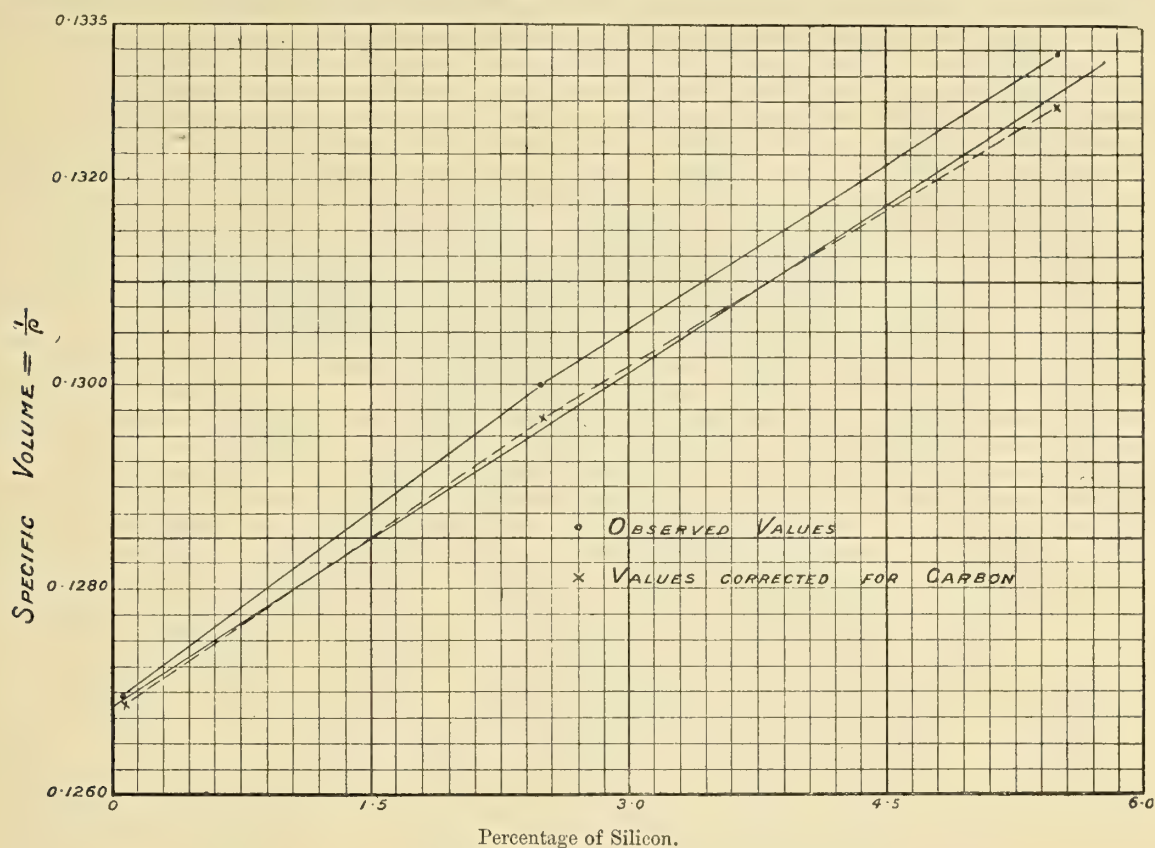
Fig. 3.—Silicon Steels.

Table VI.

Chromium Steels.

Mark	Percentage Composition		Density	Specific Volume		
	C	Cr		Observed	Calculated	Difference
993	0·90	2·00	7·7611	0·12885	0·13021	0·00136
1177 I	0·43	3·25	7·7653	0·12878	0·12910	0·00032
1177 N	1·09	9·50	7·7032	0·12982	0·13283	0·00301

In this Table are given the results obtained from three chromium steels which contain from 2 to 9·5 per cent. of chromium, the difference column showing the amount of contraction in the specific volume in each case.

If a curve be plotted having the percentage amount of chromium as abscissæ, and the specific volumes corrected for carbon as ordinates, it will be found that up to about 3·25 per cent. of chromium added to the iron the specific volume of the material is *increased*, whilst the further addition of 6·25 per cent. of chromium has no effect. The specific volume of the second specimen when corrected for carbon is 0·00112 c.c. greater than that of pure iron, and therefore the change in the specific volume of the material obtained by adding *one* per cent. of chromium to iron is at the rate of 0·00034 c.c.; so that up to about 3·3 per cent. of added chromium the specific volume of the material may be expressed as specific volume = 0·1269 + 0·00034 Cr, where Cr represents the percentage amount of chromium in the alloy; whilst the addition of higher percentages of chromium (up to at least 9·5 per cent.) has no effect on the specific volume of the alloy.

If on adding *one* per cent. of chromium to 99 per cent. of iron no change took place in the specific volumes of the constituents, then the specific volume of the alloy would be 0·00027 c.c. greater than that of pure iron; and since the observed change is 0·00034 c.c., a very slight expansion has taken place.

Table VII.

Copper Steels.

Mark	Percentage Composition				Density	Specific Volume		Difference
	C	Mn	Al	Cu		Observed	Calculated	
1264 A	0·68	0·36		1·59	7·8354	0·12763	0·12878	− 0·00115
1264 B	0·59	0·32		2·50	7·8366	0·12761	0·12837	− 0·00076
1263 C	0·17	1·04		2·87	7·8470	0·12744	0·12708	+ 0·00036
1149 A	0·04	0·16	1·00	3·75	7·7479	0·12907	0·12905	+ 0·00002

The results of four copper steels which contain from 1·59 to 3·75 per cent. of copper are given in Table VII.; and if we plot a curve having the percentages of copper present as abscissæ and for ordinates the specific volumes of the specimens corrected for the presence of carbon, manganese, and aluminium, it will be found that the effect of the addition of copper to iron is to diminish slightly the specific volume of the alloy. By comparing the corrected specific volume of the first specimen with that of pure iron, the *decrease* in the specific volume is 0·0005 c.c. for every *one* per cent. of added copper up to about 1·6 per cent. of copper; and the specific volume of the material is not appreciably changed by the further addition of copper up to about 4 per cent.

If on adding *one* per cent. of copper to 99 per cent. of iron no change were to take place in the specific volumes of the constituents, the specific volume of the resultant alloy would be about 0·00015 c.c. *less* than that of pure iron; and since the observed change was 0·0005 c.c. an expansion has occurred.

Table VIII.

Cobalt Steels.

Mark	Percentage Composition				Density	Specific Volume		Difference
	C	Mn	Si	Co		Observed	Calculated	
1209 C	0·25	1·0	0·64	1·8	7·8117	0·12801	0·12943	0·00142
1209 F	0·52	0·8	0·80	7·0	7·8326	0·12767	0·13013	0·00246

The results for two cobalt steels are here given in Table VIII.; and if we plot as before the percentage amount of cobalt present as abscissæ and the specific volumes—corrected for carbon, manganese, and silicon—as ordinates, it will be seen that a straight line drawn through these corrected values cuts the axis of ordinates practically at the value for pure iron.

We therefore find that the addition of 7 per cent. of cobalt to iron *decreases* the specific volume of the material by 0·0007 c.c., or at the rate of 0·0001 c.c. for every 1 per cent. of cobalt added. If no change were to take place in the specific volumes of the constituents when *one* per cent. of cobalt is added to 99 per cent. of iron, then the specific volume of the resultant alloy would be 0·00011 c.c. less than that of pure iron; and since the observed change is 0·0001 c.c., it seems that neither expansion nor contraction has taken place.

Table IX.

Aluminium Steels.

Mark	Percentage Composition				Density	Specific Volume		Difference
	C	Si	Cr	Al		Observed	Calculated	
803	0·67	2·25		0·50	7·5930	0·13170	0·13681	0·00511
1167 H	0·24	0·18		2·25	7·5132	0·13310	0·13396	0·00086
1178 E	0·22		1·5	4·50	7·1582	0·13970	0·14048	0·00078

In Table IX. are given the results for three aluminium steels which contain

0·5, 2·25, and 4·5 per cent. of aluminium, respectively ; and in fig. 4 the observed values of the specific volumes, as well as the specific volumes corrected for carbon, silicon, and chromium, are plotted against the percentage of aluminium present.

Percentage of Aluminium.
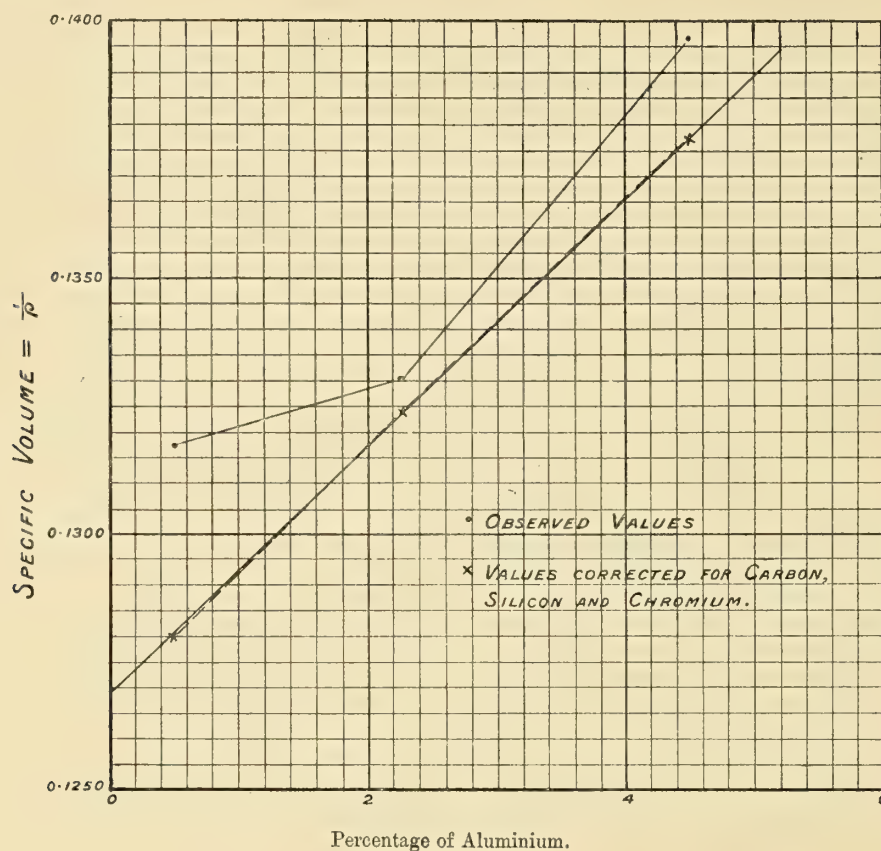
FIG. 4.—ALUMINIUM STEELS.

By drawing a mean line through the corrected points, we see that the addition of *one* per cent. of aluminium to iron *increases* the specific volume of the alloy at the rate of 0·0025 c.c. for every 1 per cent. of aluminium added, or specific volume = 0·1269 + 0·0025 Al, where Al represents the percentage amount of aluminium present.

If no change were to take place in the specific volumes of the constituents when one per cent. of aluminium is added to 99 per cent. of iron, the specific volume of the resultant alloy would be 0·00258 c.c. greater than the specific volume of pure iron ; and since the observed change is 0·0025 c.c., there is practically neither contraction nor expansion.

TABLE X.

NICKEL-MANGANESE STEELS.

Mark	Percentage Composition			Density	Specific Volume		Difference
	C	Mn	Ni		Observed	Calculated	
1109 D	0·8	5·04	14·55	7·8272	0·12776	0·12768	0·00008
1414 A	0·6	5·04	19·00	7·8542	0·12732	0·12641	0·00091
1414 B	0·6	5·04	25·00	7·9101	0·12642	0·12554	0·00088

In Table X. are given the results for three nickel steels which have each the same amount of manganese present, and nearly the same percentage of carbon. If the observed specific volumes be corrected for the presence of carbon and manganese, it will be found that these corrected points lie practically on the nickel curve in fig. 1, as might be expected from the results of the other high nickel steels given in Table III.

CONCLUSIONS.

The following are the conclusions that may be drawn from these experiments:—

1. *Carbon* when added to iron (up to about 0·2 per cent. of carbon) *increases* the specific volume of the material at the rate of 0·0018 c.c. for every *one* per cent. of carbon added, and for higher percentages of carbon—up to about 1·25 per cent. —the *increase* in specific volume is at the rate of 0·0015 c.c. per 1 per cent. of carbon present.

2. *Manganese* when added to iron (up to about 2 per cent. of manganese) *increases* the specific volume of the material by about 0·00026 c.c. per *one* per cent. of added manganese, and for higher percentages of manganese—up to about 18·5 per cent.—the specific volume is *decreased* about 0·00015 c.c. per *one* per cent. of added manganese.

3. *Nickel* when added to iron (up to 20 per cent. of nickel) has no effect on the specific volume of the material; but when between 20 and 31·4 per cent. of nickel is present, the specific volume of the material is *decreased* at the rate of about 0·00023 c.c. for every *one* per cent. of added nickel.

4. *Tungsten* when added to iron (up to about 15 per cent. of tungsten) *decreases* the specific volume of the material by 0·0009 c.c. per *one* per cent. of added tungsten.

5. *Silicon* when added to iron (up to 5·5 per cent. of silicon) *increases* the specific volume of the material by 0·0011 c.c. for every *one* per cent. of added silicon.

6. *Chromium* when added to iron (up to about 3 per cent. of chromium) *increases* the specific volume of the material by about 0.00034 c.c. per *one* per cent. of added chromium, but a further addition of chromium—from 3 up to 9·5 per cent. —has no effect on the specific volume of·the alloy.

7. *Copper* when added to iron (up to about 1·5 per cent. of copper) *decreases* the specific volume of the material about 0·0005 c.c. for every *one* per cent. of added copper; but the specific volume of the alloy is not appreciably changed by further additions of copper up to about 4 per cent.

8. *Cobalt* when added to iron (up to 7 per cent. of cobalt) *decreases* the specific volume of the material by 0·0001 c.c. for every *one* per cent. of added cobalt.

9. *Aluminium* when added to iron (up to 4·5 per cent. of aluminium) *increases* the specific volume of the material by 0·0025 c.c. for every *one* per cent. of aluminium added.

Taking the specific volume of pure iron as 0·1269 c.c., the effect of adding an element to iron is exhibited in the following table.

In column A is given the change in the specific volume of the material obtained by adding *one* per cent. of an element to 99 per cent. of iron, *assuming that no change takes place in the specific volumes of the constituents ;* the sign (+) means that the resultant specific volume is *greater* than, and (−) means that it is *less* than, the specific volume of pure iron, viz.: 0·1269 c.c. Column B gives the corresponding values obtained from these experiments.

Name of Element	Calculated A	Observed B	Difference A − B
Carbon	+ 0·00308 c.c.	+ 0·0018 c.c.	0·00128 c.c.
Manganese	+ 0·00008 ,,	+ 0·00026 ,,	0·00018 ,,
Silicon	+ 0·0029 ,,	+ 0·0011 ,,	0·0018 ,,
Chromium	+ 0·00027 ,,	+ 0·00034 ,,	0·00007 ,,
Aluminium	+ 0·00258 ,,	+ 0·0025 ,,	0·00008 ,,
Nickel	− 0·00014 ,,	− 0·00003 ,,	0·00011 ,,
Tungsten	− 0·00075 ,,	− 0·0009 ,,	0·00015 ,,
Copper	− 0·00015 ,,	− 0·0005 ,,	0·00035 ,,
Cobalt	− 0·00011 ,,	− 0·0001 ,,	0·00001 ,,

PART II.

Specific Heat.

In the determination of the specific heats of the specimens, the method of mixtures was employed, and a form of Regnault's calorimeter used, in which the body to be tested is suspended in an air chamber and heated by means of a steam jacket. The apparatus was placed well away from the boiler and screened from currents of air, and the exhaust from the steam jacket took place into the outer air by means of a pipe let through the sash of a window. This method of getting clear of the exhaust steam allowed the room to be kept at a practically constant temperature for two or three hours at a time.

The calorimeter when in use contained about 20 grammes of distilled water, and very careful experiments were made to find its water equivalent, as well as that of the thermometer and stirrer, so that 2·2 gramme-degrees were taken throughout the investigation as the water equivalent of the apparatus.

The loss by radiation was so small that no allowance was made for it, especially as the whole operation of dropping the hot body into the cold water, and the time occupied by the mixture in attaining a steady temperature, was not more than one minute.

The thermometer was graduated in tenths of a degree Cent. from 5° to 25° C., and the length of one degree on stem was 13 mm., and therefore $\frac{1}{10}$° C. was 1·3 mm., which distance could be divided by the eye, aided by a lens, into ten equal parts, so that 0·01° C. could be easily read. This thermometer was compared with a Kew standard, and found correct. An error of 0·01° C. in reading the temperature of the mixture would only affect the fourth decimal place in the value of the specific heat, and therefore the first three decimal places are taken as correct in the following tables.

The specific heats of the alloys were all determined at temperatures from 10°–13° C. and the results here given are each the mean of three or more separate experiments. The percentage chemical composition is repeated in the following tables, and the specific heat of each specimen is given, along with the thermal capacity per unit bulk.

TABLE XI.

CARBON STEELS.

Mark	Percentage Composition			Specific Heat σ	ρ × σ
	C	Si	Mn		
S. C. I.	0·028	0·07	—	0·1134	0·8933
L. S. S.	0·05	0·02	0·18	0·1136	0·8949
1166 A	0·14	0·08	—	0·1144	0·8996
1392 A	0·85	0·17	0·32	0·1192	0·9330
1392 G	1·23	0·12	0·14	0·1234	0·9612
611	0·58	0·49	0·58	0·1170	0·9142
613	1·00	0·49	0·58	0·1220	0·9466
614	1·25	0·46	0·62	0·1225	0·9497

In Table XI. are given the specific heats of the eight carbon steels, along
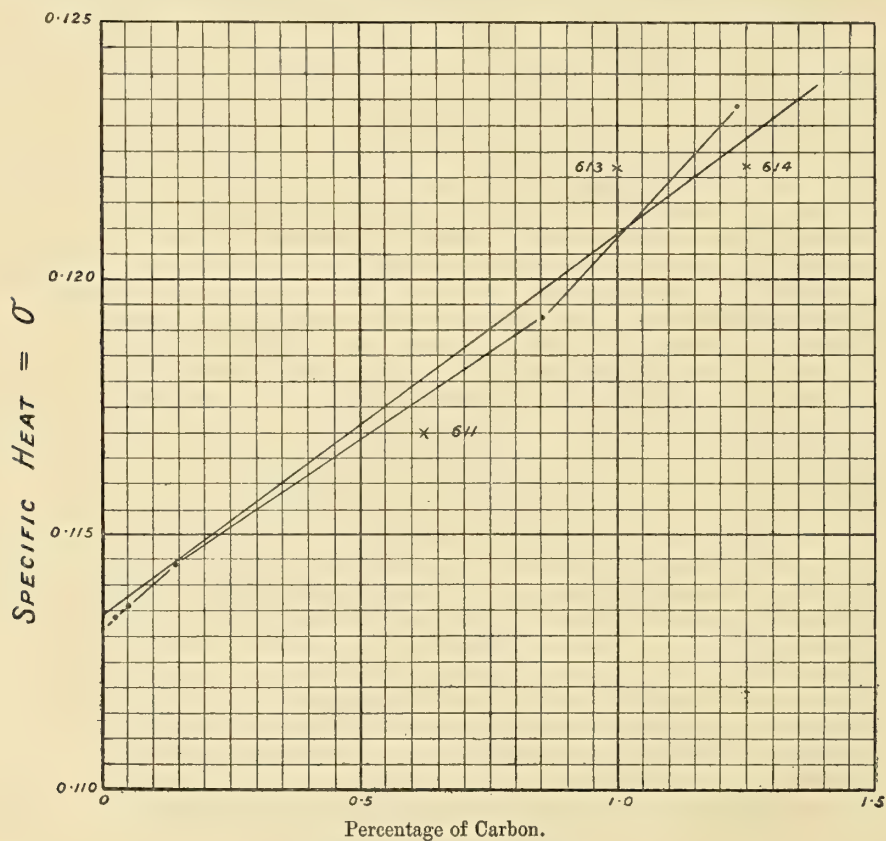
FIG. 5—CARBON STEELS.

with the product of the specific heat and density of each specimen, the densities used being those found and recorded in Part I. of this paper.

The percentages of carbon and the specific heats are plotted on a somewhat large scale in the curve, fig. 5, which shows that the presence of carbon in iron increases the specific heat of the material.

By comparing specimens S.C.I. and 1166 A it will be seen that an increase of 0·112 per cent. of carbon increases the specific heat of the material 0·001, and therefore the addition of *one* per cent. of carbon will increase the specific heat about 0·0089.

Taking an average and comparing the specimens marked 1166 A and 1392 G, it will be found that for an increase of 1·09 per cent. of carbon, the specific heat is increased 0·009, and therefore the increase for *one* per cent. of carbon is about 0·0083; or taking the mean line on the curve from 0 to 1 per cent. of carbon, the increase in the specific heat is 0·0075. If the specific heats could have been measured correctly to the fifth place of decimals, it might then have been possible to estimate more accurately the effect on the specific heat of an alloy produced by the addition of say 1 per cent. of another element to iron.

The last column in the table shows that increase of carbon in the iron increases the thermal capacity per unit volume of the material.

TABLE XII.

MANGANESE STEELS.

| Mark | Percentage Composition | | Specific Heat | $\rho \times \sigma$ |
	C	Mn	σ	
48	0·20	0·50	0·1180	0·9258
4147	0·24	1·00	0·1150	0·8987
53	0·41	2·25	0·1155	0·9007
39	0·36	4·00	0·1165	0·9128
1323 C	0·15	5·40	0·1172	0·9189
945 A	1·20	7·00	0·1184	0·9357
1338 B	0·26	13·00	0·1225	0·9796
598	1·54	18·50	0·1250	0·9884

In Table XII. are given the specific heats and thermal capacities of the eight

manganese steels, and the manganese curve in fig. 6 shows the specific heats plotted against the amount of manganese present in the specimens.

By comparing the specimen marked 48 in this table with the specimen S.C.I. in Table XI., which is practically pure iron, it would appear that by adding 0·5 per cent. of manganese to the iron the specific heat is *increased*, and adding 0·5 per cent. more of manganese decreases it, whilst after that point the addition
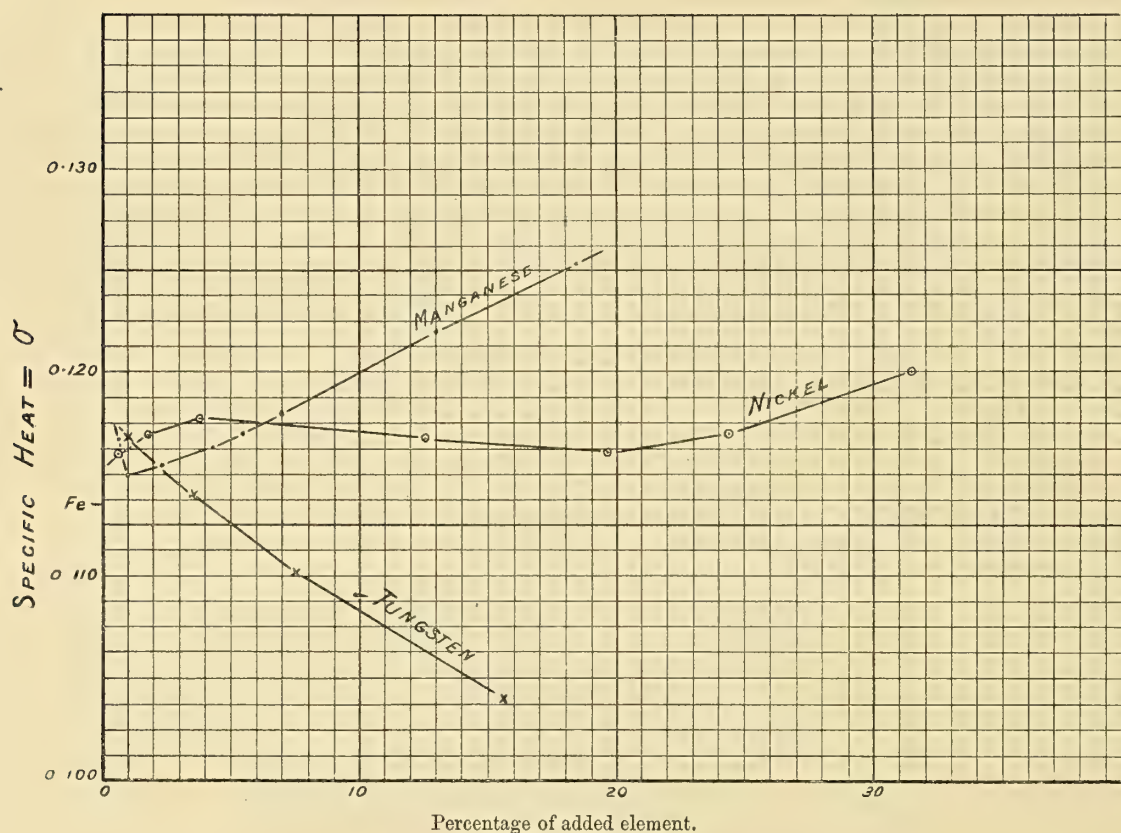
FIG. 6—MANGANESE, NICKEL, AND TUNGSTEN STEELS.

of manganese increases the specific heat at a fairly uniform rate. By comparing the specimens containing *one* per cent., and 18·5 per cent. of manganese respectively, it is seen that 17·5 per cent. of manganese added to iron increases the specific heat by 0·01. Also for the same percentage range of manganese, the thermal capacity per unit volume is increased at a nearly uniform rate, as shown in the last column of Table XII.

TABLE XIII.

NICKEL STEELS.

| Mark | Percentage Composition | | | | Specific Heat | |
	C	Si	Mn	Ni	σ	$\rho \times \sigma$
1397 B	0·26	0·33	0·18	0·58	0·1156	0·9051
1287 D	0·14	0·21	0·72	1·92	0·1171	0·9213
1287 E	0·19	0·20	0·65	3·82	0·1180	0·9271
1447 A	0·81	0·39	0·61	12·70	0·1170	0·9120
1287 K	0·19	0·27	0·93	19·64	0·1157	0·9124
1287 L	0·16	0·30	1·00	24·51	0·1170	0·9282
1449 A	0·70		0·82	31·40	0·1209	0·9707

In Table XIII. are given the specific heats and thermal capacities of the seven nickel steels, and in the nickel curve fig. 6 the specific heats are plotted against the percentage amounts of nickel present. From the curve it will be seen that the specific heat of the alloy is *increased* up to about 4 per cent. of nickel present; then a slight *decrease* occurs until about 20 per cent. of nickel is reached; then up to about 31 per cent. the specific heat is again *increased*.

This point of flexure in the curve of the nickel steels, when about 20 per cent. of nickel is present in the iron, occurs in the case of the other physical properties of these specimens so far tested, viz., in the electrical, the magnetic, and the mechanical,* as well as in the density.

By comparing the first specimen in Table XIII. with the pure iron S.C.I. in Table XI., we see that the first addition of 0·58 per cent. of nickel to the iron increases the specific heat of the material by 0·0022, or at the rate of about 0·0038 for every 1 per cent. of added nickel; and comparing the two specimens containing 0·58 per cent. and 3·82 per cent. of nickel respectively, it will be seen that the addition of 3·24 per cent. of nickel increases the specific heat by 0·0024. By comparing the specimens marked 1287 E and 1287 K it is seen that the addition of about 16 per cent. of nickel decreases the specific heat 0·0023, and between 20 and 31 per cent. of nickel, the specific heat is increased by 0·005.

The last column in Table XIII. shows that the presence of about 31 per cent. of nickel increases the thermal capacity per unit volume by about 6·75 per cent.

* Scient. Trans. Roy. Dublin Soc., 1900, vol. vii., pp. 111, 112.

Table XIV.

Tungsten Steels.

| Mark | Percentage Composition | | | Specific Heat | |
	C	Mn	W	σ	ρ × σ
1294 F	0·16	0·11	1·0	0·1162	0·9222
1294 H	0·28	0·28	3·5	0·1136	0·9161
1294 I	0·38	0·20	7·5	0·1100	0·9121
1294 L	0·76	0·28	15·5	0·1041	0·9131

In Table XIV. are given the specific heats and thermal capacities of four tungsten steels; and in the tungsten curve, fig. 6, the specific heats are plotted against the percentage of tungsten present. These results show the remarkable effect of a high percentage of tungsten when added to iron, in diminishing the specific heat of the material. Taking the specific heat of pure iron as 0·1134, the addition of one per cent. of tungsten appears to increase the specific heat by 0·0028, and for higher percentages the specific heat is decreased.

By comparing the first and last specimens, it is seen that the addition of 14·5 per cent. of tungsten to iron that already contains 1 per cent. of tungsten decreases the specific heat of the material by 0·0121, or about 10·4 per cent. And since tungsten added to iron *increases* the density and *decreases* the specific heat, the thermal capacity per unit volume is very nearly constant, as will be seen from the last column of Table XIV.

Table XV.

Silicon Steels.

| Mark | Percentage Composition | | Specific Heat | |
	C	Si	σ	ρ × σ
S. C. I.	0·028	0·07	0·1134	0·8933
898 E	0·20	2·50	0·1200	0·9232
898 H	0·26	5·50	0·1194	0·8967

In Table XV. are given the results for two silicon steels, with which is put that

of the pure iron S.C.I. for comparison. From the first two specimens in the table, it would appear that the addition of 2·43 per cent. of silicon increases the specific heat of the material about 0·0066, or at the rate of very nearly 0·003 for every *one* per cent. of added silicon; whilst a further addition of 3 per cent. of silicon has very little effect on the specific heat.

And since silicon added to iron *decreases* the density and *increases* the specific heat, the thermal capacity per unit volume remains fairly constant, as indicated in the last column of Table XV.

Table XVI.

Chromium Steels.

Mark	Percentage Composition		Specific Heat	
	C	Cr	σ	$\rho \times \sigma$
993	0·90	2·00	0·1202	0·9329
1177 I	0·43	3·25	0·1169	0·9078
1177 N	1·09	9·50	0·1206	0·9290

The results for the three chromium steels in Table XVI. are somewhat irregular, the effect of the chromium on the specific heat being masked by the high percentage of carbon present. Judging from the first and third specimens, which have approximately the same amount of carbon, the specific heat is not altered by the addition of 7·5 per cent. of chromium. The effect is probably entirely due to carbon, seeing that in the case of the second specimen, marked 1177 I, the amount of carbon is about half of that in the other two specimens, and its specific heat is reduced. In fact, if the results for these chromium steels are plotted on the plate, fig. 5 of the carbon steels, they will all lie very nearly on that curve, showing that chromium has little or no effect on the specific heat of the iron when a high percentage of carbon is present.

Table XVII.

Copper Steels.

Mark	Percentage Composition				Specific Heat	
	C	Mn	Al	Cu	σ	$\rho \times \sigma$
1264 A	0·68	0·36		1·59	0·1180	0·9246
1264 B	0·59	0·32		2·50	0·1180	0·9259
1263 C	0·17	1·04		2·87	0·1178	0·9244
1149 A	0·04	0·16	1·00	3·75	0·1173	0·9088

The results for the four copper steels are here given in Table XVII., and in this case also the effects of the copper on the specific heat seem to be masked by the carbon present; in fact, the results for the first two specimens practically lie on the carbon curve in fig. 5.

In the third specimen marked 1263 C with a less amount of carbon, but with a higher percentage of manganese, the specific heat is practically the same as in the first two specimens, showing that the copper present has little or no effect on the specific heat. The last specimen in Table XVII. contains 1 per cent. of aluminium; and, judging from the aluminium steels in Table XIX., below, the presence of 3·75 per cent. of copper seems to raise the specific heat a little.

The last column in Table XVII. shows that the thermal capacity per unit volume is fairly constant.

Table XVIII.

Cobalt Steels.

Mark	Percentage Composition				Specific Heat	
	C	Mn	Si	Co	σ	$\rho \times \sigma$
1209 C	0·25	1·0	0·64	1·80	0·1153	0·9007
1209 F	0·52	0·8	0·80	7·00	0·1157	0·9062

The results of the two cobalt steels in Table XVIII. show that cobalt added to iron has very little effect on the specific heat when there are other elements present.

In the first specimen the carbon—as in the case of the chromium steels—seems to dominate the action of the cobalt as well as that of the manganese and silicon, since the result for this specimen also lies on the carbon curve in fig. 5.

In the second specimen the increase in the specific heat that would be expected from the increased amount of carbon present seems to be counteracted by the extra 5·2 per cent. of cobalt. These specimens, however, are not pure enough to enable one to draw from their results any definite conclusion; but it would appear that cobalt added to iron diminishes the specific heat. The thermal capacity per unit bulk is also fairly constant in these specimens.

Table XIX.

Aluminium Steels.

Mark	Percentage Composition				Specific Heat σ	$\rho \times \sigma$
	C	Si	Cr	Al		
803	0·67	2·25		0·50	0·1158	0·8793
1167 H	0·24	0·18		2·25	0·1165	0·8753
1178 E	0·22		1·5	4·50	0·1195	0·8554

In Table XIX. are given the results for three aluminium steels containing from 0·5 to 4·5 per cent. of aluminium. They also contain fairly large proportions of other elements, and are not pure enough to warrant any definite conclusions being drawn from their results. Taking, however, the purest specimen, marked 1167 H, and comparing it with the pure iron S.C.I. in Table XI., and assuming that the increase in the specific heat due to adding 1 per cent. of carbon to iron is 0·0083, and that the increase for the addition of 1 per cent. of silicon to iron is 0·0029, then on correcting the specific heat of the specimen 1167 H for carbon and silicon it becomes 0·1139, which is practically that of pure iron, so that the addition of 2·25 per cent. of aluminium to iron does not appear to alter practically its specific heat.

The last column in Table XIX. shows that the thermal capacity per unit volume is decreased nearly 3 per cent. by the addition of 4 per cent. of aluminium.

TABLE XX.

Nickel-Manganese Steels.

Mark	Percentage Composition			Specific Heat	
	C	Ni	Mn	σ	ρ × σ
1109 D	0·8	14·55	5·04	0·1208	0·9455
1414 A	0·6	19·00	5·04	0·1194	0·9378
1414 B	0·6	25·00	5·04	0·1186	0·9402

The three steels in Table XX. contain each a high percentage of carbon, as well as over 5 per cent. of manganese; and if the results are plotted on the high nickel part of the nickel curve in fig. 6, the points all lie above it; and they also lie a little above the carbon curve in fig. 5. The combined action of carbon and manganese, no doubt, masks the effect of the nickel on the specific heat. The thermal capacity per unit bulk remains fairly constant, as shown in the last column of the Table.

Conclusions.

The following conclusions may be drawn from these experiments:—

1. *Carbon* added to iron increases the specific heat by about 0·0089 per 1 per cent. of added carbon.

2. *Manganese*, when added to iron up to about 18 per cent., increases the specific heat about 0·0006 per 1 per cent. of added manganese.

3. *Nickel*, when added to iron up to 4 per cent., increases the specific heat 0·0038 for every 1 per cent. of nickel added; and further additions of nickel up to 20 per cent. have little or no effect, whilst between 20 and 31 per cent. of nickel the specific heat is increased by 0·005.

4. *Tungsten*, when added to iron up to 1 per cent., *increases* the specific heat 0·0028; and when 3·5 per cent. of tungsten is present, the specific heat of the material is the same as that of pure iron; whilst a further addition of 12 per cent. of tungsten decreases the specific heat by 0·0093.

5. *Silicon*, when added to iron up to about 2 per cent., increases the specific heat

by 0·003 for every 1 per cent. of added silicon; but further additions of silicon have little or no effect.

6. *Chromium, Copper,* and *Cobalt,* when separately added to iron, have very little effect on the specific heat when a high percentage of carbon is present.

7. *Aluminium,* when added to iron up to about 3 per cent., seems to have little or no effect on the specific heat.

PART III.

In 1899 a paper on the magnetic properties of these alloys was read before this Society,* in which the energy dissipated per cycle was given for some of these steels. It will, therefore, be of interest to apply the results now obtained for the densities and specific heats, and to calculate the temperature rise in the iron when subjected to a series of cycles, as in commercial work. We will take two cases— (1) the teeth in the armature core of a direct current dynamo, and (2) the core of an alternating current transformer. The frequency of the magnetic flux in the armature of a direct current dynamo is seldom higher than 20 per sec., and the induction about 16000 c.g.s. lines, and in transformers the mean induction employed in practice is 6000 c.g.s. lines at a frequency of 50 per sec.

In the following table are given the temperature rise in degrees centigrade for *one hour,* and the energy dissipated per cycle in the two cases, as well as the principal constituent in each alloy other than the iron.

The values in the fifth column for the energy dissipated have been calculated from those in the third column by means of Steinmetz's formula.

Assuming that all the heat produced by hysteresis remains in the iron, we have

$$\theta = \frac{\frac{1}{4\pi}\int H \cdot dB}{J\rho\sigma}$$

when the numerator of the fraction expresses the energy dissipated per complete cycle, and J = Joule's equivalent 42×10^6 ergs, ρ = the density of the material, σ = the specific heat, and θ = the temperature rise in degrees centigrade.

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* Barrett, Brown, and Hadfield. Scient. Trans. Roy. Dublin Soc., 1900, vol. vii., pp. 67–126.

TEMPERATURE RISE IN DEGREES CENTIGRADE DUE TO HYSTERESIS IN ONE HOUR.

Mark	Principal Constituent	Induction = 16000 c.g.s. Frequency = 20 per sec.		Induction = 6000 c.g.s. Frequency = 50 per sec.	
		Energy dissipated per cycle	Temperature Rise	Energy dissipated per cycle	Temperature Rise
S. C. I.	0·028 C	10000	19° C	1908	9·2° C
B.	0·03 C	11000	21	2090	10·2
L. S. S.	0·05 C	11460	22	2180	10·5
611	0·58 C	22810	43	4620	21·7
48	0·50 Mn	20460	38	2290	18·4
4147	1·00 Mn	23080	44	4710	22·5
1287 D	1·92 Ni	15750	29	3050	14·2
1287 E	3·82 Ni	16300	26	3086	14·3
1294 F	1·00 W	14580	31	2865	13·3
1294 H	3·50 W	25800	48	5170	24·3
1167 H	2·25 Al	10950	21	2170	10·6
898 E	5·50 Si	6500	12	1290	6·2

In both cases the advantage of the silicon iron or steel over pure iron is shown by these results. A silicon iron is now extensively used for armature and transformer cores, and is known commercially as Stalloy. For sheets of thickness 0·356 mm. the energy loss at an induction of 6000 c.g.s. lines and frequency 50, is 0·38 watt per lb. as compared with 0·58 watt per lb., the value for practically pure iron under the same conditions.

As far as I know, the chemical composition of Stalloy has not yet been made public; but from the tests which I recently made of the specific volume of this material, I should say that it contained about 3·3 per cent. of silicon.

In conclusion, I beg to state that my best thanks are due to Professor Barrett, F.R.S., who has afforded me every facility for carrying on this work in a Laboratory where space for private research is very limited.

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VII.

AN INVESTIGATION OF THE CONNEXION BETWEEN BAND AND LINE SPECTRA OF THE SAME METALLIC ELEMENTS.

[PLATES I. AND II.]

BY

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VII.
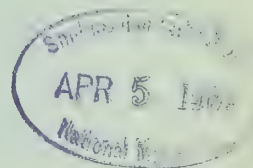
AN INVESTIGATION OF THE CONNEXION BETWEEN BAND AND LINE SPECTRA OF THE SAME METALLIC ELEMENTS.

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PLATES I., II.

PART I.

INTRODUCTION.

In three papers, published in the years 1882-83,* the connexion between the atomic weights, the chemical properties, and the spectra of the elements was pointed out, and the law of constant differences was demonstrated in the intervals between the lines in the spark spectra of magnesium, zinc, cadmium, also copper and silver. In conformity with the periodic law it was found that the line spectra of different groups of elements were spectra similarly constituted, from which it was deduced that they are produced from similarly constituted molecules containing the same kind of matter in different states of condensation. As only monatomic molecules were under consideration, it was believed that the atoms were composed of parts, and that as more of these definite parts were contained in one volume of the vapour, the mass of the atom increased by a definite quantity, and in any well-defined homologous group the elements possessed gradational differences in properties.

In another series of papers† the nature and constitution of various flame-spectra were examined, and it was shown that many metals have two distinct

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* Jour. Chem. Soc., "Note on certain Photographs of the Ultra-violet Spectra," &c., **41**, 84, 1882; "On Homologous Spectra," **41**, 390, 1883; "On the Spectrum of Beryllium," &c., **42**, 316, 1883.

† "Flame-Spectra at High Temperatures," Phil. Trans., 1894, **185**, part I, pp. 161–212; Parts II. and III., pp. 1029–1091; and 1901, **196**, pp. 479–506; also Hartley and Ramage, Sci. Trans. Roy. Dublin Soc., 1901; **7** Series, pp. 339–352.

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spectra, one composed of lines, the other of bands. The band spectra of the metals were observed to be subject to regular variations in structure, some of which were evidently connected with the periodic law in such a manner as to point to a similarity in molecular constitution; and, furthermore, certain spectra which had been attributed to oxides were in reality the spectra of the metals. Elements belonging to the same group emit band spectra with characters in common, e.g. copper, silver, and gold in the sub-group of the monad metals; calcium, strontium, and barium in the sub-group of the dyad metals; also tin and lead in the tetrad group. The bands of silver in the flame-spectrum appeared to be related to the principal lines of the element in the same way that a band spectrum of a gas at 760 mms. pressure becomes a line spectrum when the pressure is reduced to 7 mms. or less.

In fact, it was found that in the spectra of lead, silver, and copper, the lines seen in the heads of bands, or overlaid by bands, were, in nearly every case, the only parts of the complex band spectrum remaining, after any one of these metals had been diluted with some other metal.

The effect of reduced pressures upon the arc spectrum of iron affords* an illustration; it is a simple line spectrum at a pressure of 17 mms. of mercury, but as the pressure increases, a continuous spectrum is also seen in the region of rays less refrangible than λ 5300 and in a less intense degree, between λ 4700 and λ 4300. The same effect is seen in the oxyhydrogen flame spectrum of iron, and in the Bessemer flame-spectra, when in either case the vapour-pressure of the iron is reduced.

In nearly every case the lines seen in flame spectra after the bands have disappeared correspond with reversed lines in the arc, and are the most persistent lines in the spark spectra of the same element. Although it was believed that they are not absolutely identical, they must have a common origin, for they occur as constituent lines of homologous groups, and they have so very nearly the same wave-lengths and persistency as the corresponding lines in the arc and spark, that no substantial difference has been found between them.

In endeavouring to account for two distinct spectra being obtained from the same metal, by heating in the same manner, and in some instances to approximately the same temperature, it was observed that the phenomena were such as would arise from the presence of two distinct substances in the flame, such as a metal and its oxide,† or by the reduction of the vapour-pressure of the substance, the bands being caused by the greater vapour-pressure in the flame

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* J. E. Petavel and R. S. Hutton, Phil. Mag., **6**, 569, 1903.

† Allotropic forms of the same substance according to Plücker and Hittorf, the allotropy depending, however, solely upon temperature.

than when the spectrum consisted of lines. Opposed to this view was the fact mentioned by Kayser, that in the arc there must have been a larger quantity of silver than that contained in the oxyhydrogen flame, when the spectrum of the metal in each case was under observation; nevertheless, from the arc, lines without bands were photographed (Kayser's Handbuch der Spectroscopie, vol. ii., pp. 258 and 286, 1902), and it was suggested that the band spectrum and the continuous background of rays[*] observed in many flame-spectra might be accounted for by the flame containing unusually large atom-complexes, or molecular aggregates. In the case of monatomic molecules the vapour-densities of which are known,[†] this appears to be inconceivable; for it is difficult to imagine a substance such as cadmium or zinc with a monatomic constitution, which is known in each case from its vapour-density, at a temperature well above its boiling point, to consist of molecular aggregates and not of simple molecules. At the same time it must be admitted that the remarks concerning the vapour-pressures of silver in the flame and arc respectively were very difficult to answer satisfactorily : first, because there are good reasons for doubting whether the vapour-pressure in the arc referred to by Kayser was actually greater than in that part of the flame where silver is being boiled freely and continuously, the vapour being condensed like a cloud, and deposited on surrounding objects ; and again, the conditions under which the vapour is produced in the arc and in the flame may be very different. The banded spectra both of tin and of silver were observed in the arc by Liveing and Dewar, and, more recently, A. Hagenbach[‡] has shown that the arc may be made to yield both band and line spectra, even the spectra of compounds such as chlorides. The researches of Kayser and Runge, also of Rydberg, have reduced the constitution of line spectra in definite groups of the elements to a mathematical expression, of which the respective atomic weights are a function ; but the spectra are of a comparatively simple constitution, the band spectra of the same elements being more complicated. Both bands and lines of the same element may often be obtained in the same flame ; silver and copper afford examples of this. The bands are numerous and complex ; but the lines, common to the flame, arc, and spark, are not. Thus the cause of the difference between the band and line spectra would appear, in the absence of further evidence, to be mainly a difference in temperature. That the bands are the spectrum of the

[*] For a recent investigation see Proc. Roy. Soc., 1906, A., vol. **78**, p. 403, " Note on the Continuous Rays observed in the Spark Spectra of Metalloids and some Metals."

[†] Von Wartenberg (Metallurgie, 1906, 39, 381) has shown that from the relative density of silver vapour at 2000°, the molecule is monatomic.

[‡] " Ueber Banden-Spectra." Festschrift. Aachen. June 1905. B. G. Teubner, Leipzig.

element, and not that of a compound, is evident in the case of silver, from the following facts:—

1st. The band spectrum is easily produced directly from the metal in the oxyhydrogen flame.

2nd. It is not an oxide spectrum, because silver oxide cannot exist at such a temperature, and the same spectrum has been obtained by Basquin by means of the arc in an atmosphere of hydrogen.

3rd. It is not a hydride spectrum, because silver hydride is decomposed at 440°, and the spectrum can with equal facility be photographed from metallic silver heated in the oxygen and carbon monoxide flame. Another method of obtaining such spectra is that of Gouy, improved by de Watteville, by burning a mixture of coal-gas and air under pressure, the air conveying spray from a solution of a salt into the interior of a number of small jets of flame which burn with a green cone and a blue mantle. De Watteville has photographed the spectra of many elements produced in this manner,* but he mentions that with some metals, the flame spectrum contains bands of a more or less complicated character, in addition to the lines, and he has tabulated only the lines.

In the paper " On Homologous Spectra " it was pointed out that Sir Norman Lockyer† had proposed to explain the occurrence of coincident lines in the spectra of different elements by supposing that each spectrum is composed of several spectra, and that these compound spectra are the spectra of compound bodies, and not of elements; but as this hypothesis is scarcely compatible with homology in the structure of spectra, belonging to certain well-defined groups of elements in the periodic system of classification, it was suggested that, instead of single coincident lines, homologous groups of lines should be sought for. With this object in view the wave-length measurements of about 2,500 lines in the spark spectra of the elements‡ were closely examined. The majority of the substances had been prepared especially in a state of great purity, and twelve of those concerning which any doubt was entertained underwent a special examination. The result led to the detection of similarly constituted groups of lines in some of the spectra (copper and tellurium, for example), which were subsequently shown to have their origin in impurities in the elements. It was also observed that by the method of experimenting employed, the lines of impurities, when present in small proportions, appeared at one electrode only, and were therefore easily recognized and identified.

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* Phil. Trans., 1904, **204**, 139-68.   † Proc. Roy. Soc., **28**, 157, 1865.

‡ Hartley and Adeney, Phil. Trans., 1884.

I have recently returned to this line of investigation in order to ascertain the connexion between these bands and lines which undoubtedly belong to the same element, and are a characteristic feature of its spectra. It is necessary to eliminate the spectra of compounds, and to avoid confusion with hydrides and halides, which on the one hand might be formed in the oxyhydrogen flame, or, in the case of chlorides, left undecomposed.

In the continuation of former experiments, made with the object of determining the actual weights of salts necessary for the formation of bands and lines respectively in the same flame, results were obtained which had not been anticipated. First, the spectrum reaction proved to be much less sensitive in several instances than it is generally believed to be. Secondly, the lines were not found to gradually merge into bands, as at first appeared to be the case, for the band spectra appeared independently of the lines, rather as if they belonged to entirely different substances. The lines did not invariably appear before the bands: that is to say, with a smaller quantity of substance in the flame, sometimes they appeared simultaneously with them, and with some substances they appeared after the bands were extinct. In other words, the first evidence of the presence of a substance in the flame was the appearance of a banded spectrum, and then subsequently, when the quantity of a substance had been increased, particular lines, probably the fundamental vibrations of the element, began to appear. Thirdly, a background of continuous rays, observed in certain of the flame-spectra, have been proved to be traversed by a number of bands.

The following is an account of observations on the quantitative relations between the substances examined and the spectra photographed or otherwise recorded. Experience showed that only pure substances should be used when it is possible to obtain them.

Reference may be conveniently made to a communication recently submitted to the Royal Society on this subject. Part I. dealt with the banded spectra of alkali and alkaline earth metals, and the proofs based upon chemical grounds that these are the spectra of the metals.

Part II. consisted chiefly of a discussion of the thermo-chemistry of flame reactions and the colouration of the flame. In these discussions it was necessary to give evidence of the temperatures employed, and these, it may be remarked, were measured by the melting point of pure platinum. The temperatures of the flames were shown to lie between $1775°$ and $2000°$.

There were other facts taken into account, such as the facility with which tin, lead, iron, nickel, and cobalt are vapourized, the two first copiously; and the boiling of silver and gold, with their subsequent condensation on objects placed near to or in the flame; also that weighed quantities of iridium and palladium were volatilized in the flame in the same manner, and their spectra photographed.

Evidence of the reduction of refractory oxides to the state of metal was obtained from the occurrence of groups of metallic lines in their spectra.

The calcium group of elements is of particular interest in this connexion, because their band-spectra have hitherto been generally attributed to compounds such as oxides or chlorides, but evidence incompatible with this view is deduced from the following facts:—

(1) The flame-spectrum of metallic calcium is substantially the same as that from calcium oxide.

(2) The oxides and carbonates give no spectrum in the carbon monoxide flame, or in the flame of carbon monoxide when burnt with oxygen.

(3) The oxides and carbonates of the alkaline earths yield very brilliant spectra when ignited in the flame of burning cyanogen, which are identical with those obtained with the oxyhydrogen flame ; and in the case of calcium with the spectrum obtained from that metal.

(4) The chlorides yield very similar if not identical spectra when ignited in the carbon monoxide flame, and the spectra are particularly brilliant.

(5) Cupric oxide, which is easily reduced to copper in the oxyhydrogen flame, and yields the complex banded spectrum of the metal, gives only a very feeble spectrum of bands in the carbon monoxide flame, along with the pair of lines which belong to the oxyhydrogen flame-spectrum.

This is evidence of the bands being the spectrum of the metal and not of the oxide.

(6) Ferric oxide yields ninety lines, inclusive of five or six sharply defined edges of bands, in the oxyhydrogen flame-spectrum ; the lines of this spectrum appear as reversed lines in Kayser and Runge's arc spectrum of iron, and also in the solar spectrum measured by Rowland.

On submitting ferric oxide to the action of the carbon monoxide and oxygen flame, the same groups of lines are photographed, in the same order of relative intensities, but the lines in the whole spectrum are weaker than in the oxyhydrogen flame ; when the conditions as to oxidation and reduction are modified by the carbon monoxide being burnt from the oxygen jet in the interior of the flame, the oxygen being supplied to the outer tube of the blow-pipe, so that the reducing gas is burnt in a powerfully oxidizing atmosphere, a similar spectrum is photographed.

The inferences to be drawn from these experimental results are two : first, though the temperature is sufficiently high in the Mecke burner to melt platinum ($t = 1775°$), and is even higher than this in the carbon monoxide flame, the maximum temperature is confined to a smaller area of the flame than admits

of a sufficient quantity of the metal being reduced and vapourized, so as to yield a spectrum with so great an intensity as to be visible, or to be photographed; secondly, though there can be no great difference between the temperatures obtained in the Deville blow-pipe flame when supplied with oxygen and hydrogen, or oxygen and carbon monoxide, yet the reducing power of the oxyhydrogen flame under the conditions which obtain in the flame exceeds that of carbon monoxide. The reason of this is evident from an investigation by A. Gautier (C.R. 1906, **142**, 1382) of the reduction of water-vapour by carbon monoxide. The temperature at which it occurs is from 1200° to 1250°.

Equilibrium is established between the reacting substances when the volume of hydrogen is double that of the carbon monoxide, in the sense of the following equation :—

$$3\ CO + 2H_2O = 2CO_2 + 2H_2 + CO.$$

The reduction of CO_2 proceeds at 1300°, and the conditions of equilibrium are then represented as follows :—

$$CO_2 + 3H_2 = CO + H_2O + 2H_2.$$

This latter equation shows that coal-gas may be substituted for pure hydrogen in the oxyhydrogen blow-pipe, but this has not been found to be satisfactory in practice ; and it also affords an explanation why a filter-paper may be burnt in the flame without interfering with the reduction to metal caused by the hydrogen gas.*   At or from 1200° to 1400°, or at a white heat, $CO_2 = CO + O$ is the rule, for even at 1250° carbon monoxide deposits carbon in a porcelain tube.

This conclusion receives confirmation from the facts observed with regard to the reduction in the oxyhydrogen flame of various refractory metallic oxides.

Most closely allied to calcium, strontium, and barium is magnesium. Kainite, $K_2SO_4 \cdot MgSO_4 \cdot MgCl_2 \cdot 6H_2O$, and kieserite, $MgSO_4 \cdot H_2O$, both equally strongly show the magnesium flame-spectrum as given in " Banded Flame-Spectra of Metals," p. 343, and observed in 1888, by Liveing and Dewar, when magnesia was heated in the oxyhydrogen flame.

The lines and bands recorded on my photographs of kainite and kieserite are the following :—λλ 5209, triplet 5184, 5174, 5168 : a group of six so-called "oxide bands"—1st, 5004, 2nd 4993, 3rd 4988, 4th 4971, 5th 4960, 6th 4944 : also strong bands from λλ 4100 to 3700.   Hence it is impossible to believe that this spectrum is not the spectrum of metallic magnesium, for the first of the above lines, viz.: 5209 (L. and D. 5210), was obtained by the spark from a solution of

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* If many filters are burnt, the effect upon the spectrum is similar to that observed when coal-gas instead of hydrogen is supplied to the blow-pipe, that is to say, there is a strong continuous spectrum due to the burning of carbon monoxide. The combustion of at least ten filter-papers is necessary to show this.

magnesium chloride in a Delachanel and Mermet's tube ; it is also at the head of the magnesium-hydrogen band.

The lines of the triplet are common to arc, spark, and the flame of burning magnesium.

The experiments of Liveing and Dewar have proved beyond all question that magnesium oxide is reduced by three different reactions : in the oxyhydrogen flame, in the flame of cyanogen when burnt in oxygen, and of carbon monoxide mixed with half its volume of oxygen, and burnt as it issues from the gas-holder (Proc. Roy. Soc., 1888, **44**, 241). The bands are called the "oxide bands," because, as Liveing and Dewar pointed out in their second paper (1888), p. 242, "they are due either to magnesia, or to the chemical action of oxidation," and again on p. 248, "the triplet near *M* and its associated bands" are due, "not to merely heated magnesium, but to the oxide, or to vibrations set up by the process of oxidation."

The same remark, based upon similar experimental evidence, applies to "*calcium oxide*" bands, also to the bands observed in the oxyhydrogen flame-spectra of strontium and barium oxides,* that is to say, they are due to vibrations set up probably by the chemical process of oxidation. To return to magnesium, it has been stated by Olmsted that he has found no strong band corresponding to that observed by me in 1894 in the magnesium sulphate spectrum, between the

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* It is necessary that this should be clearly stated, because the term has not been applied in this sense by recent investigators; thus, de Watteville remarks on the occurrence of bands with magnesium, barium, strontium, calcium, copper, tin, and manganese : "The study of these bands, and the nature of the compound to which they are due, forms no part of the present investigation."

Since the publication of my paper "On the Thermo-Chemistry of Flame-Spectra at High Temperatures" (Proc. Roy. Soc., A, vol. **79**, 1907), two communications have been made upon the subject of Bunsen flame-spectra by Carl Fredenhagen (Phys. Zeitschr., 1907, **8**, 407–415, and Ber. 1907, **40**, 2858–2861). They are considered by the author to be the result of chemical reactions, and not solely the effect of a high temperature, as I have already shown. The argument employed is, that they are always obtained in oxygen flames, but not in the hydrogen-chlorine flame; hence the spectrum reaction is due to the union of the metals with oxygen. In support of this contention, Smithell's modified Bunsen burner (Chem. Soc. Trans., 1982, **61**, 204) was fed simultaneously with lithium and copper salts, by employing Beckmann's method, which is in effect that of E. Cleminshaw (Phil. Mag. [5], **19**, 365–368, 1885). It is found that the outer zone of the flame is coloured green, while the inner zone is coloured red. This is accounted for by the copper being oxidized in the outer zone, but not in the inner ; but the lithium having a greater affinity for oxygen than hydrogen, is oxidized in the inner zone. The proper interpretation may be exactly the opposite, the copper oxide being reduced in the outer zone, and the lithium only at the higher temperature of the inner zone; but, as de Watteville has shown, both series of lines may appear in the green flame of the inner zone.

It is evident that the proofs I had given, of the manganese bands belonging to the element, and not to its oxide, had been overlooked by de Watteville. Also C. M. Olmsted, "Die Bandenspektra nahe verwandter Verbindungen," Zeitschr. f. wissenschaft. Photographie, 1906, **4**, 255, refers to the bands of MgO, CaO, &c.

wave-lengths 3856 and 3929, and therefore believes that it belongs to the magnesium sulphate itself. The spectrum was photographed not only from the sulphate but also from dolomite, and from the nitrate, which is converted into magnesia in any ordinary flame with the greatest ease. The particulars with regard to this band, and a comparison with those near *L* and *M*, observed by Liveing and Dewar, are given on p. 210 of "Flame Spectra at High Temperatures." It consists of a group of so-called "*oxide bands*," which by a prolonged exposure has become a nearly continuous spectrum. But even if the particular spectrum referred to by Olmsted were obtained from the sulphate, this salt would have been instantly converted into the oxide, and subsequently into the metal.

EXPERIMENTAL.—PART I.

The Purification of Barium and Strontium Salts.

A hot saturated solution of barium chloride is poured slowly in a gentle stream into a quantity of strong hydrochloric acid, the mixture being stirred, pure barium chloride is precipitated, which may occupy one-third the volume of the liquid. The treatment may then be repeated. The salt is separated from the acid on a parchment paper-filter by a filter-pump, and washed first with small quantities of dilute hydrochloric acid, then with a minimum of cold distilled water, and finally with alcohol. The salt so prepared is dried in a silver basin. A similar treatment of strontium chloride, owing to its greater solubility, is modified by passing gaseous hydrochloric acid into the cold aqueous acid mixture, after the strontium salt has largely deposited.

Other salts were prepared from the carbonates, which were obtained by precipitation with pure ammonium carbonate, from solutions of the dissolved pure chlorides. The most impure commercial salt is generally the strontium chloride; that which has been sold as *pure* contained in one sample as much as 30 per cent. of calcium chloride. Other metals have been separated in the manner described from different specimens of strontium salts and from strontianite, namely—iron, manganese, copper, nickel, yttrium, traces of cerium, and zinc. Calcite of great purity is purchasable, and this may be dissolved, any iron oxidized, ammonium chloride and ammonia added, the solution filtered and the carbonate repre-cipitated.

On the quantities of Salts rendering Band and Line Spectra.

It is necessary when solid substances are wrapped in ashless filter-papers* and burnt in the oxyhydrogen blowpipe flame, that the roll of paper be introduced into

* Hartley and Ramage, Chem. Soc. Trans., 1901, **79**, 61.

the hottest part, that is to say very near to the point of the inner cone of the flame, which proceeds from the nozzle delivering the oxygen, otherwise the peculiar and distinguishing character of the spectrum may escape being photographed; for instance, the continuous rays and subordinate series of lines in the potassium spectrum may fail to appear, or the blue line of lithium, and one in the ultra-violet, may be wanting.

The treatment of soluble salts is described in the following notes, this being somewhat different from the treatment of solid substances, insoluble compounds, or elements.

Lithium.

An alcoholic solution of pure fused lithium nitrate was prepared, containing 0·0069 gr. of metallic lithium in 1·0 c.c. of alcohol. The requisite quantity of solution was delivered, from a graduated pipette reading to $\frac{1}{100}$ of a cubic centimetre, on to an ashless filter-paper 10 cms. in diameter; ten of such papers when burnt showed feebly only the sodium spectrum, with no trace of the lines of lithium. The paper was dried in an air-bath, and the dried filter was cut into strips about 3 cms. broad; these strips, being very tightly rolled up spirally, were burnt slowly, with the highest temperature obtainable in the oxyhydrogen flame. The flame measured 12·5 cms. × 1·8 cms. when illuminated by the substance. Edwards' Isochromatic plates were used, which were developed with "imogen sulphite."

Description of the Spectrum photographed.

Quantity of Lithium.

Quantity of Lithium	Description
0·0131 gr.	The following lines were observed, measured and identified. The wave-lengths varied but slightly from those more accurately measured by Ramage; his figures are given.* λλ 4603·07, 4132·93, and 3232·82 their intensities varied with the quantity of substance.
0·0110 gr.	
0·0096 gr.	
0·0089 gr.	λλ 4132·93 and 3232·82. These lines became weak.
0·0082 gr.	The line λ 4603·07 alone was visible.
0·0041 gr.	
0·0020 gr.	No line visible, except the red λ 6708.

The results show that when the most persistent line λ 4603·07 is photographed, there cannot be less than 4 mlgrs. of lithium in the flame during the period of exposure; similarly, when three lines are photographed, there cannot be less than

* Proc. Roy. Soc. **71**, 164–71.

8·9 mlgrs. present. Ramage has shown that, with the exception of 6103·84, the lines in the first subordinate series have wave-lengths, which differ by + 0·28 to + 0·70 from those in the arc as measured by Kayser and Runge, and that this element appears to behave exceptionally in this respect; hence his numbers are quoted.

POTASSIUM.

Pure dry potassium nitrate was dissolved in water, in the proportion of 2·6 grs. to 100 c.c. of the solvent. This is equivalent to 1 gr. of potassium. Absolute alcohol and water were added alternately until the volume of the solution became 500 c.c. without precipitating any of the salt: 1 c.c. of this solution thus contained 0·002 gr. of potassium. Edwards' Isochromatic plates were used. With the first quantity of substance, a somewhat complicated spectrum was obtained.

Quantity of Potassium.	*Description of the Spectrum photographed.*
0·5 gr.	A triplet λλ 5832·25, 5802·12, 5782·74. A band of diffused rays from λ 5782·74, increasing in intensity to λ 5554, and decreasing to λ 5376. A triplet λλ 5376, 5359·96, 5340·17. Two lines λλ 5217, and 5124. A strong band from λ 4895, continuing with the same intensity to the fine pair of lines of potassium, and a third one belonging to manganese, seen in the violet λλ 4047·39, 4044·33, and (4041·5 manganese), continuing with gradual weakening to about λ 3300. In this band a line appears λ 3447·56.
0·004 gr. ⎫ 0·0036 gr. ⎬ 0·0032 gr. ⎭	Feeble bands are seen corresponding to those described above. A strong line λ 4047·39 and a feeble line λ 3447·56.
0·0024 gr.	The line λ 3447·56 has disappeared, and the band of continuous rays is very feeble.
0·0020 gr. ⎫ 0·0016 gr. ⎬ 0·0012 gr. ⎭	Line λ 4046 is strong, but is really composed of 4047·39 and 4044·33, and the manganese line (4041·5); the first and the last are the most prominent.
0·0006 gr. ⎫ 0·0004 gr. ⎪ 0·0002 gr. ⎬ 0·0001 gr. ⎭	The line alone visible is λ 4047·39.
0·0000016 gr. ⎫ 0·0000008 gr. ⎭	The line λ4047·39 is still visible, but it disappears when one-half the last quantity, or 0·0000004 gr., of potassium is taken.

The very sensitive character of the potassium spectrum explains why so large a number of minerals, and also of precipitates obtained in analytical processes, have been found to contain traces of potassium. Thus in 169 various ores and minerals not supposed to contain this element, potassium was found.*

CALCIUM.

Spectra were photographed from (a) solid salts of calcium ignited in the oxyhydrogen flame, from (b) calcium metal burning in the flame of a Mecke burner, from (c) particles of lime in the same flame, and from (d) the condensed spark passed between electrodes consisting of thin plates of metallic calcium, and (e) the spark without condenser, taken from solutions. Eye observations were made of the spark without condenser, passing from solutions of known strength. The wave-lengths are approximations only, though obtained from actual measurements on the photographs. They closely approximate in many cases to the measurements of the lines made by Eder and Valenta in the spectrum of the spark, and of Kayser and Runge in the arc. It must be noted that the measurements of the flame spectra do not appear to coincide with those of calcium oxide recorded in "Flame Spectra at High Temperatures," notwithstanding their having a common origin. To account for these differences it must be understood that the latter measurements were made from the edges of bands, and the wave-lengths might differ widely, owing to variations in the spectra caused by the width of the slit, the dispersion employed being too small, the duration of exposure too long, and the quantity of substance introduced into the flame being large. In the earliest experiments, the dispersion was that of only one-quartz prisms of 60°, but subsequently a spectrograph with four prisms was in constant use. It is certain that the exposure of the plates in the one-prism instrument was unnecessarily prolonged, both bands and lines being obscured by the great density of the photographs.

Calcium—Oxyhydrogen Flame Spectrum.

Calcium nitrate, prepared from an especially pure precipitated calcium carbonate, was dissolved in alcohol, and made of such a strength that 1 c.c. corresponded to 0·004 gr. of calcium. Isochromatic Seed plates were used.

The following lines were visible, but less refrangible lines were not photographed, the plates being less sensitive to the red than to the green rays :—

Quantity of Calcium.

0·0028 gr. 0·0020 gr.	λλ 5543, 5517, and 4226·99.
0·0016 gr.	The lines visible were λλ 5543 and 5517.
0·0014 gr.	No lines visible.

* Hartley and Ramage, Journal of the Iron and Steel Institute, 1897.

The lines 5543 and 5517 are probably components of an exceedingly strong band, extending from 5598 to 5485, but they correspond with two spark lines measured by Eder and Valenta. The red band with centre at λ 6223 was not photographed on this plate.

Calcium—The Flame of the Burning Metal.

Metallic calcium was rolled out into thin sheets, from which slips about 3 mms. in width were cut and burnt in the flame of a Mecke burner. The flame was focussed on to the slit of the spectrograph. Wratten and Wainwright's panchromatic plates were used.

Quantity of Calcium.

Description of the Spectrum photographed.

2·45 gr.   The red line of lithium λ 6078, and the yellow lines Na¹ and Na² of sodium were visible, but generally the two latter appeared as one line. The quantity of lithium could not have exceeded 0·002 gr.

The red, orange, and green bands of calcium were broad and dense. A feeble band of continuous rays extended to a little beyond λ 4226·9. The line λ 4226.9 was dense and broadened out near its base; it tapered off to a fine point towards the apex of the flame. It was the only strong line seen. There was absolutely no trace of lines corresponding to the great and intense H and K lines λ 3968·6 and λ 3933·8, common to the arc and condensed spark. The lines about λ 4455, 4435, and 4586 appeared very short and feeble, barely visible in fact.

0·50 gr.   I. The red, orange, and green bands only appeared, and these were feeble. The impurity lines of lithium and sodium were seen.

0·50 gr.   II. Photographed with a finer slit the red, orange, and green bands were proved to be composed of fine narrow bands very close together.

III. A bead of calcium chloride was heated in the flame, until all that remained was calcium oxide. This was left in the flame of a Mecke burner until nothing but a very feeble tinge of red was visible.

The spectrum consisted of the red band with centre at λ 6223, and the green band with centre at λ 5534 of calcium, with the impurity lines of sodium between them. The exposure lasted about three hours, during which time the substance in the flame was not renewed.

IV. *The Spectrum of Calcium as obtained from Lime.*

To compare with the preceding spectra, a bead of fused calcium nitrate was placed in the flame of a Mecke burner of the smallest size. When all evolution of gas had ceased, the bead of lime was placed in the middle of the flame, and about 3 mms. above the grating of the burner, which is the point where the highest temperature can be communicated to an object of the size of the bead on the platinum loop.

The lime was white hot, and it appeared as if translucent. The flame was coloured a pure pale red. Measurements were made with the eye of the edges of bands and strong rays. The bands seen were two in the red, one in the orange, and one in the green. The spectrum was identical with those numbered I. and III. The plates used were Wratten and Wainwright's panchromatic.

Calcium—Flame Spectra : Mecke Burner.

Description of Spectra.

			Mecke Burner with Air Blast.	Mecke Burner without Air Blast.
			λ	λ
1st.	Deep red band,	l. r. edge,	$\begin{cases}6482 \\ 6395\end{cases}$ m. r. edge,	$\left.\begin{array}{l}6469 \\ 6376\end{array}\right\}$ very feeble diffuse band.
				$\left.\begin{array}{l}6280 \\ 6200\end{array}\right\}$ 1st component.
2nd.	Strong red band,	l. r. edge,	$\left\{\begin{array}{l}6225 \\ \text{to} \\ 6098\end{array}\right.$ m. r. edge,	$\left.\begin{array}{c}\text{feeble} \\ \text{to} \\ 6158\end{array}\right\}$ 2nd component.
				$\left.\begin{array}{c}\text{very} \\ \text{feeble} \\ \text{to} \\ 6150\end{array}\right\}$ 3rd component.
3rd.	Orange band,	l. r. edge,	$\begin{cases}6037 \\ 5935\end{cases}$ m. r. edge,	$\left.\begin{array}{l}6050 \\ 5964\end{array}\right\}$
4th.	Green band,	l. r. edge, A component of the band, m. r. edge,	$\left\{\begin{array}{l}5555 \\ 5534 \\ 5514\end{array}\right.$	$\left.\begin{array}{l}5555 \\ 5534 \\ 5515\end{array}\right\}$ strong components. less strong.

In these two spectra, in which the bands of the one are wider than those of the other, the sole difference in the mode of producing them caused a larger

amount of substance to be vapourized in the blast flame. The temperature is naturally higher and the area of maximum temperature larger. In the plain Mecke burner the first or deep red band is feeble and diffuse; it is apparently continuous with the second red band, which, in turn, is seen to have three component bands. There are similarly three component bands in the green band.

Spectrum obtained from the Spark without Condenser.

These were observations made many years ago with solutions of known strength, contained in Delachanel and Mermet's fulgurator. When solutions are used, the same quantity of material is exposed between the electrodes again and again, so that in viewing the spectrum with the eye the average brilliancy is observed, and not the aggregate effect as on a photograph. Standard solutions of pure calcium salts were made, containing 1·0, 0·1, 0·01, and 0·001 per cent. of the metal. The spectra were not photographed.

Where the number in the preceding column of the following tabulated statement is repeated, this is indicated by an asterisk in place of the figures.

Description of Spectrum.

PROPORTIONS OF CALCIUM IN SOLUTION.

	1·0 per cent.	0·1 per cent.	0·01 per cent.	0·001 per cent.
A band,	{ 6460 6436 }	{ * appears as a short line. * }	{ * * }	6460 appears as a short line.
A narrow band,	{ 6348 6320 }	{ * * }	{ * * }	
A broad band,	{ 6265 6203 6161 }	{ * * * }	{ * * * }	6265
	{ 6068 6044 }	{ * * }	{ * * }	6068
An orange band.		The orange band has vanished.		
	5933	{ 5933 appears as a short line. }	5933 a short line.	
	5534 5517	{ * * }	{ * * }	{ 5534 5517 }
Greenish diffuse band.				
A line.	4226·9	4226·9	{ 4226·9 appears as a short line. }	4226·9 a short line.

There is a similarity between this spectrum and those obtained by means of the Mecke burners, with and without the air-blast.

The greatest difference occurs with the solution containing 0·001 per cent. of calcium, as in this case the bands have been reduced to lines.

Spectrum with a Condensed Spark taken from Metallic Calcium.

Eder and Valenta examined and published an account of the spark-spectrum of calcium, and by reference to this the lines have been identified. (K. Akad. Wissenscht. Wien. **77**, 1898).

The wave-lengths of the lines have been adopted from their memoir. Wratten and Wainwright's panchromatic plates were used. Thirty-four lines were counted between λ 6499·9 and λ 3624.

STRONTIUM.

Oxyhydrogen Flame Spectrum.

Strontium nitrate was dissolved in alcohol in such proportion that 0·00876 gr. of strontium was contained in 1 c.c. of the solution. Photographed with Wratten and Wainwright's panchromatic plates.

Weight of Strontium.	Description of Spectrum photographed.
0·0175 gr.	Lines visible λλ 6086, 6053, 4607.
0·0087 gr.	Only one line visible λ 4607.
0·0043 gr.	Only one line visible λ 4607.
0·0035 gr.	Nothing visible.

Strontium—Spark without Condenser.

These spectra were not photographed, but observed by the eye, the sparks being taken from solutions in a fulgurator.

Description of Spectrum.

PROPORTIONS OF STRONTIUM IN SOLUTION.

2·0 per cent.	1·0 per cent.	0·1 per cent.	0·01 per cent.	0·001 per cent.
6747	*	6747		
6627	*	Band diffuse.		
6497	*	6497	6497	6497
6364	*	Band.		
6243 Band.	*	6243 a line.		
6053	*	Band.		
6031	*	6031 a fine line.	6031	6031
Band composed of fine lines in the green. { 5541 5524 5504 5480 5448	* * * *	A band; the component lines are not distinguishable.		

	2 per cent.	1 per cent.	0·1 per cent.	0·01 per cent.	0·001 per cent.
Band composed of three lines. {	5255	—	—		
	5239	—	—		
	5225	—	—	A band extending to the last group, the components of which are not distinguishable.	
	4964	—	—		
	4607	—	—		
	4215	—	—		
	4077	—	—		4670

BARIUM.

Oxyhydrogen Flame Spectrum.

Re-crystallised barium chloride was dissolved in the proportion of 4·884 grs. of $BaCl_2 2H_2O$ in 100 c.c. of water. This contained 2·74 grs. of barium. Photographed with Wratten and Wainwright's panchromatic plates.

Description of Spectrum Photographed.

Weight of barium.

0·0996 gr. { Fluted bands extending intermittingly from λ 5380 to λ 4080, and strong lines about λλ 5274, 5180, and 4900·1.
There is also a strong line at λ 5536.

0·0822 gr. { Fluted bands from λ 5780 to λ 4080, with strong lines λλ 5274, 5180, and 4900. A strong line at λ 5536.

Weight of barium.

0·0548 gr. { Fluted bands growing weak, but extending from λλ 5720 to 4420, with lines λλ 5274, 5180, and 4900.   A strong line at λ 5536.

0·0274 gr. { The fluted bands are weak and extend from λλ 5720 to 4640.   The lines λλ 5274, 5180, and 4900 are still visible.

0·0164 gr. { Bands very feeble, the lines λλ 5274 and 5180 are hardly visible; λ 4900 is feeble.   The line λ 5534 is strong.

0·0137 gr. { The line λ 4900 is very faintly visible, and that at λ 5536 is weak. The bands and other two lines have quite disappeared.

0·0109 gr.   Lines λλ 4900 and 5536 are barely visible.

0·008 gr.   No trace of the spectrum.

The line λ 5536, sometimes recorded as 5535, corresponds with 5535·69, a strong reversed line in Kayser & Runge's arc-spectrum; it was found by de Watteville to be the strongest line both in the flame and the cone when the spray was barium chloride solution.   It seemed probable that the bands of barium chloride might be found in the flame spectrum taken from the chloride, but only the very narrow bands or lines, with wave-lengths 5274, 5180, and 4900 belong to the compound.   The first of these is apparently a band corresponding to one measured at its centre by Olmsted[*] at 5242·2 ; the second with one at 5168·9; the third does not appear in Olmsted's spectrum, the nearest approach to it being at λ 5066, which is very weak.

Spark Spectrum without Condenser.

This spectrum was not photographed.

Description of Spectrum.

Proportions of Barium in Solution.

1·0 per cent.	0·1 per cent.	0·01 per cent.	0·001 per cent.
5535	*	5535	5535
5318	*	—	—
5242	*	—	—
5136	*	—	—
4932	*	4932	4932

Two green lines here; not measured.

| 4556 | 4556 | 4556 | — |

[*] " Die Bandenspektra nahe verwandter Verbindungen." Charles Morgan Olmsted. Zeitschrift f. wissenschaftl. Photographie, vol. iv., p. 255, 1906.

The spectrum of copper is also given in detail as photographed.   Its behaviour is very similar to that of the alkaline earth metals; that is to say, almost to the last trace of substance in the flame the spectrum is a band spectrum with two lines. The bands in the spectrum are also of two kinds, the composite bands apparently composed of fine lines, and the simple bands of diffused rays.

This spectrum disappears when there is less than 6 mlgrs. of copper in the flame.   Photographed with Wratten and Wainwright's panchromatic plates.

Copper.

Oxyhydrogen Flame Spectrum.

A standard solution of cupric nitrate, $Cu(NO_3)_2 \cdot 3H_2O$, was made by dissolving 2·416 grs. of the salt in 100 c.c. of water.

Weight of Copper.

0·25 gr.   A fluted band spectrum, characteristic of metallic copper, is visible from λ 5745, increasing to greatest intensity about λ 5520, and extending with diminishing intensity to its disappearance about λ 4300.   A pair of lines is visible in the band λλ 3274 and 3247.

0·01908 gr.   A strong band extends from λ 5560 to λ 5605.   The two lines λλ 3274 and 3247 are visible in the band.

0·01272 gr.   The band is feeble.   The lines λλ 3274 and 3247 are visible.

0·00636 gr.   The band is almost invisible.   The two lines are still visible.

0·00318 gr.   Nothing visible.

The spectra of the alkali metals at the highest temperature of the oxyhydrogen flame, and those obtained from the arc, more nearly resemble each other than do any other two spectra yielded by the same element.   For instance, the following doublets in the sodium spectrum have been photographed as single lines from a variety of salts placed in the flame :—

| 6161·1 } | 5896·2 } | 5688·3 } | 5153·7 } | 4893·5 } | 4669·4 } | 3301·1 } |
| 6154·6 } | 5890·2 } | 5682·9 } | 5149·2 } | 4979·3 } | 4615·2 } | 3302·5 } |

But by reducing the quantity of substance in the flame, some of the lines have been photographed as double, for instance, the two yellow lines ; where the space between them measured 0·45 mm., the difference in wave-lengths was 6 Ångström

uni018s.   This conveys some idea of the dispersion and the fine definition of the lines photographed with the four-prism quartz-spectrograph.

Similarly in the potassium spectrum, the following groups have been photographed as distinct lines, but with the separation of the lines into doublets, or triplets in some cases, when the quantity of substance in the flame was reduced.

5832·23 ⎫	5359·88 ⎫	5112·68 ⎫	4047·36 ⎫	3447·49 ⎫
5802·01 ⎬	5340·08 ⎬	50 99·64 ⎬	4044·29 ⎭	3217·76 ⎭
5782·67 ⎭	5323·55 ⎭	4870·4 ⎭		

PART II.

Further experiments devised for the purpose of ascertaining the conditions under which the bands of different characters are emitted by the flame spectra of the elements rubidium, cæsium, calcium, strontium, barium, silver, and copper; and likewise to trace the origin of the bands.

The coefficients of extinction of bands and lines respectively, in the spectra of the same elements, were obtained by burning gradually diminishing quantities of salts of the metals in the oxyhydrogen flame. For example, in the case of silver, 3·1 grs. of crystallized $AgNO_3$ (= 2 grs. Ag) were dissolved in 20 c.c. of absolute alcohol. Proportionate volumes of this solution were then dropped on to ashless filter-papers, and when dry were burnt in the flame in the usual manner. But it was necessary also to use larger quantities of some of the salts than could be satisfactorily ignited in this manner in one operation. In such cases the dry solid compound was employed: sometimes this was burnt on filter-paper; in other instances it was introduced on slips of kyanite. Care was taken not to prolong the time occupied by the combustion or ignition, because this is tantamount to extending the period of exposure of the plate, and to elucidate the desired facts this would be inadmissible. It must be understood, however, that when 2 grs. of the alkali salts were ignited, it was necessary to take four filter-papers, which quadrupled the period of exposure when only 0·5 gr. was ignited. This may be considered as the maximum of difference.

All the following spectra were photographed on Wratten and Wainwright's panchromatic plates, when not otherwise stated.

Rubidium.

The salt used was RbCl. Photographed with Wratten and Wainwright's panchromatic plates.

Quantity of Rubidium.

Description of Spectrum.

2 grs.   There are three characteristic features in this spectrum: 1st, a continuous spectrum, composed in part of fine lines, about the region of wave-length 4700; 2nd, a diffuse band appears in the red between λ 7000 and λ 6700; 3rd, lines. The measurements here quoted are those made by H. Ramage on photographs taken from oxyhydrogen flame-spectra (Proc. Roy. Soc., 1902, vol. **70**, p. 308). Several of the weaker lines do not appear on this spectrum, all the lines of which were independently measured, and are described.

Lines.	λ	λ (Ramage).	Intensity.
A very strong pair.	7950·46 ⎫ (Lehmann. 7805·98 ⎭ arc.)*	7799	Very strong.
A very strong pair.	7699·3 ⎱ K. 7665·6 ⎰ Impurity.		
A very feeble line.	7414		
Faint.	(2790 ?)		
Faint.	6934 K ⎫		
Faint.	6902 K ⎭ Impurity.		
Faint.	6710	6306.8	1
Intensely strong pair, degraded towards the red.	6299 6207	6299·19 6206·74	9 8
Very strong.	6160	6160·04	5
Strong.	6071	6070·04	4
	Sodium lines.		
A very faint pair.	5802 K ⎫ 5786 K ⎭ Impurity.		
Very strong pair.	5726	5724·62	8
	5654	5654·16	3
		5648·19	7
Very faint.	5580	5579·3	2
Strong.	5432	5432·05	6
Faint.	5394	5391·3	1
Strong.	5362	5363·15	5
Very faint.	5341 K. Impurity.		
Very faint.	5324	5322·83	1
Strong.	5264	5260·51	4
Very faint.	5239	5234·6	1
Strong.	5193	5195·76	3
Very faint.	5166	5165·35†	2
Faint.	5149	5151·20	2
		5132·0	1
Very feeble pair.	5084 ⎱ 5071 ⎰	5089·5 5076·3	1 1
		5037·0	1
		5023·0	1
		5017·0	< 1
Very faint. (A pair ?)	4990	4983·0	< 1
	A diffuse band occurs here.	4967·0	< 1
Faint.	4590 Cs ⎱ Impurity.		
Fairly strong.	4552 Cs ⎰		
Very faint.	4389 ⎱ 4371 ⎰		
An intensely strong pair.	4217 ⎱ 4204 ⎰	4215·68 4202·04	9 10
A faint broad line.	4179 K. ?		
An intensely strong pair.	4043 ⎱ K. Impurity. 4038 ⎰		
‡An intensely strong pair.	3590 ⎱ 3586 ⎰	3591·86 3587·27	3 4
‡Strong.	3448	3350·98	1
Very faint.	3350 ⎱ Pair.	3348·84	2
†Strong.	3347 ⎰		
Very faint.	3300 Na. Impurity.	3259·26	1
		3228·18	1

* Ann. der Physik, 1901, vol. v., p. 633.

† The isolated line λ 5165·35 is narrow and sharp; it differs thus from all other lines in the series.

‡ There is an obvious discrepancy here. The lines in this spectrum marked "intensely strong" and "strong" are represented in the spectrum measured by Ramage by three weak lines.

Quantity of
Rubidium.

(1) 0·5 gr. in
　　　5 portions.

Description of Spectrum.

Lines.		Intensity.
λ		
7799		
	7699·3 ⎫ K. Impurity.	
	7665·6 ⎭	

λ (Ramage).

6299·19		9
6206·74		8
5724·62		8
5654·16 ⎱		3
5648·19 ⎰		7
5432·05		6
5363·15		5
5260·51		4
4215·68		9
4202·04	(4044) K. Impurity.	10
3591·86		3
3587·27		4

(2) 0·1 gr.　　The red band is almost extinct.

Lines.
λ

7799	⎰7950·46⎱ Lehmann. Rather strong.	
	⎱7805·98⎰	
	⎛7699·3 ⎞ Impurity. K.	
	⎝7665·6 ⎠	
6299·19	Faint.	
6206·74	Faint.	
5724·62	Faint.	
5648·19	Very faint.	
5432·05	Very faint.	
5363·15	Very faint.	
4215·68 ⎱	Very strong. (4044) Impurity. K.	
4202·04 ⎰		
3591·86 ⎱	A faint pair.	
3587·27 ⎰		

(3) 0·01 gr.　　No band.　The red lines ⎰7950·46⎱ are very feeble.
　　　　　　　　　　　　　　　　　　⎱7799·0 ⎰

Lines.
λ

6299·19	Very faint.
4215·68 ⎱	Strong. (4044) Impurity. K.
4202·04 ⎰	

(4) 0·001 gr.　No red lines.

Lines.
λ

4215·68 ⎱	Strong. (4044) Impurity K.
4202·04 ⎰	

(5) 0·0001 gr.

Lines.
λ

4215·68 ⎱	Feeble. (4044) Impurity. K.
4202·04 ⎰	

(6) 0·00001 gr.

Lines.
λ

4215·68 ⎱	Very faint. (4044) Impurity. K.
4202·04 ⎰	

<div align="center">

Rubidium.

</div>

Quantity of Rubidium.

(1) 2·0 grs. in 5 portions.　　The spectrum is continuous and very intense. The banded spectrum of fine lines is well shown between λ 5100 and 4400.

(2) 1·0 gr. in 3 portions.

(3) 0·5 gr. in 2 portions.　　There is an indication of the bands described above in both these spectra.

(4) 0·1 gr.　　No bands. The line-spectrum, as previously described, is strong.

<div align="center">

Cæsium.

</div>

CsCl was the salt used. Photographed with Wratten and Wainwright's panchromatic plates.

Quantity of Cæsium.

<div align="center">

Description of Spectrum.

</div>

2 grs.　　A continuous spectrum without bands, but with many lines. Measurements of all the lines in the flame are compared with those of Ramage (Proc. Roy. Soc., 1902, vol. **70**, p. 304).

The line λ 6984 observed by Ramage does not appear.

Lines.	λ	λ (Ramage).	Intensity.
	7805·98 Rb. Impurity.		
	7665·6 K. Impurity.		
A feeble pair.	7290		
	7236		
A very strong broad line, degraded towards the red.	6973	6984	6
A fairly strong pair.*	6866	6974	9
	6822	6869	2
Pair, very strong,* de-graded towards the red.	6730	6829	2
	6712	6722	9
Feeble. ⎫ A pair of	6630	6630	2
Fairly strong. ⎬ fine lines.	6590	6590	8
A pair of feeble fine lines.	6472	6472	2
	6433	6433	2
Fairly strong, degraded towards the red.	6356	6354	8
Very faint, diffuse.	6334		
Very faint, diffuse.	6295 Rb. Impurity.		

* The fairly strong pair is represented by two faint lines in the spectrum photographed by Ramage; and the pair, very strong, corresponds with only one line, the wave-length of which is the mean of the two.

Lines.	λ	λ (Ramage).	Intensity.
		6217·6	2
Very strong, degraded towards the red.	6214	6213·33	8
Very faint. }A pair.	{6034	6034·43	4
Very strong.}	{6010	6010·59	8
Sodium lines here.			
		5847·86	2
A very strong fine line.	5843	5845·31	8
		5839·33	2
A very faint fine line.	5748	5746·37	1
A pair of very strong fine lines.	{5664	5664·14	7
	{5635	5635·44	5
	5578	5574·4	1
		5568·9	1
A fairly strong pair of fine lines.	{5503	5503·1	3
	{5466	5466·1	4
Faint.	5417	5414·4	1
		5407·5	1
A very feeble pair.	{5351	5351·0	1
	{5341	5341·15	3
Faint.	5304	5304	< 1
Faint.	5258	5256·96	1
		5209	< 1
Faint.	5198	5199	< 1
Very faint.	5154	5154	< 1
Very faint.	5118		
Very faint.	4804		
Faint.	4762		
An intensely strong pair.	{4596	4593·3	8
	{4556	4555·46	10
Very faint.	4526		
Faint.	4229 Ca. Impurity.		
A strong pair.	4218 }Rb. Impurity.		
	4205 }		
Very faint pair.	4043 } K. Impurity.		
	4038 }		
A very strong pair.	{3885	3888·75	2
	{3873	3876·31	4
Very faint.	{3615	3617·79	< 1
Strong.	{3610	3611·70	2
Very faint.	3585		
Faint.	3477	3477·25	1
Very faint.	3399	3398·4	1
Very faint.	3300 Na. Impurity.		
		3348·72	< 1
		3314·0	< 1
		3287·0	< 1

(1) 0·5 gr.,   A continuous spectrum, no bands.
in 5 portions.

A large number of lines was photographed, of which the following
are the strongest.   H. Ramage (Proc. Roy. Soc., 1902, vol. **70**, p. 304).
The line λ 6984 observed by Ramage does not appear.

Lines. λ	Intensity.		
6974	9		
6722	9	(6298·7) Impurity. Rb.	
6010·59	8		
5845·31	8		
5664·14 }	7		
5635·44 }	5		
4593·30 }	8 }	A pair ; very strong.	$\begin{pmatrix}4215\\4202\end{pmatrix}$ Impurity. Rb.
4555·46 }	10 }		
3888·75 }	2 }	A strong pair.	By comparison with the intensity numbers of Ramage, these lines are all feeble instead of being, as here described, strong.
3876·31 }	4 }		
3611·70	2	Strong.	

(2) 0·1 gr.

Lines. λ		
6974		
6722		
6010·59		
4593·30 }	A strong pair.	
4555·46 }		
3888·75	Very feeble. }	A pair.
3876·31	Strong. }	
3611·70	Feeble.	

(3) 0·01 gr.

λ	λ	
6974 and 6723·6 are very feeble.		
4593·30 }	Strong.	
4555·46 }		
3876·31	Feeble.	

(4) 0·001 gr.

λ	
4599·30 }	Strong.
4555·46 }	

(5) 0·0001 gr.

λ	
4593·30 }	Feeble.
4555·46 }	

(6) 0·00001 gr.

λ	
4593·30 }	Feeble.
4555·46 }	

In larger Quantities.

(1) 2 grs. Cs. in 5 portions.   A strong continuous spectrum devoid of bands.
All the lines recorded above appear strongly.

(2) 1 gr. Cs. in 3 portions.
(3) 0·5 gr. in 2 portions. } The continuous spectrum is weakened,
(4) 0·1 gr. in 1 portion.   but the line spectrum is strong.

No bands similar to those in the rubidium, potassium, sodium, and lithium spectrum were photographed, but only a strong continuous spectrum.

Calcium.

The salt used was $Ca(NO_3)_2$.   Oxyhydrogen flame spectrum.   Photographed with Wratten and Wainwright's panchromatic plates.

Quantity of Calcium.

(1) 0·5 gr.   A spectrum of strong bands in the red, orange, and green ; five
in 5 portions.   of which are less refrangible than the sodium rays.

I.—Red.	II.—Red.	III.—Red.	IV.—Red.	V.—Orange.
6880 ⎱ feeble.	6778 ⎱ fairly	6568 ⎱ strong.	6346 ⎱ very	6062 ⎱ strong.
6822 ⎰	6614 ⎰ strong.	6394 ⎰	6122 ⎰ strong.	5966 ⎰

Two bands in the green, one very broad and intense, the other less refrangible, being narrow and not so strong.

VI.—Green.   VII.—Green.

5774 ⎱   5617 ⎱
5746 ⎰ narrow.   5578 ⎰ two component.

5565 ⎱
5514 ⎰ bands very strong.

Lines. λ		Eder and Valenta's measurements of the spark-lines, for comparison.	Intensity.	
4455 4435	} a pair ; feeble.	{ 4454·919 { 4435·838	10 10	
4226·9	very strong.	4226·870	10	reversed.
3969 3933	} a pair ; feeble.	{ 3968·638 { 3933·803	80 100	solar line, H. ,, ,, K.

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Hagenbach and Konen do not give these pairs of lines in the flame spectrum of calcium, but they occur in the arc and spark; the last two correspond to the solar lines H & K.

A continuous but feeble spectrum extends from the green to about λ 3640.

It is remarkable that the only lines observed on the photographs previously taken from flame spectra were 4226·87 and 4454·9.

Quantity of Calcium.

(2) 0·1 gr. on 1 paper.   The bands are strong, the two least refrangible have become faint. The orange band $\begin{Bmatrix} 6030 \\ 5964 \end{Bmatrix}$ and the strong green band $\begin{Bmatrix} 5555 \\ 5515 \end{Bmatrix}$ are each seen to be composed of two bands.

The line λ 4226 appears strong, but the two pairs of lines have entirely disappeared.

(3) 0·01 gr. on 1 paper.   The two least refrangible bands in the red $\begin{Bmatrix} 6880 \\ 6822 \end{Bmatrix}$ and $\begin{Bmatrix} 6778 \\ 6614 \end{Bmatrix}$ have quite disappeared, and the narrow green band $\begin{Bmatrix} 5774 \\ 5746 \end{Bmatrix}$ is very faint. The other bands and the line 4226 are strong.

(4) 0·001 gr. on 1 paper.   Two bands, one in the red $\begin{Bmatrix} 6280 \\ 6150 \end{Bmatrix}$ and one in the green $\begin{Bmatrix} 5555 \\ 5515 \end{Bmatrix}$, are still strong; the others have vanished. The line λ 4226 is fairly strong.

(5) 0·0001 gr.   No spectrum.

(6) 0·00001 gr.   No spectrum.

The bands in the oxyhydrogen flame spectra of calcium are degraded towards the violet, and where a band is seen to be composed of two narrower component bands, the stronger of the two is the less refrangible.

STRONTIUM.

The salt used $Sr\,(NO_3)_2 \cdot 4H_2O$.

Description of Spectrum.

Quantity of Strontium.

(1) 0·5 gr. in 5 portions.

A continuous spectrum, consisting of a series of bands in the red, green, violet, and ultra-violet, with some lines.

I.—Red.	II.—Red.	III.—Red.	IV.—Red.
$\left.\begin{array}{l}7102\\6982\end{array}\right\}$ feeble.	$\left.\begin{array}{l}6878\\6782\end{array}\right\}$ feeble.	$\left.\begin{array}{l}6766\\6548\end{array}\right\}$ strong.	$\left.\begin{array}{l}6530\\6382\end{array}\right\}$ intense, composed of two narrow bands.

V.—Red.	VI.—Orange.	VII.—Yellow and Green.	VIII.—Green.
$\left.\begin{array}{l}6310\\6238\\6178\end{array}\right\}$ strong.	$\left.\begin{array}{l}6120\\6008\end{array}\right\}$ intense.	$\left.\begin{array}{l}5838\\581_2\end{array}\right\}$ feeble.	$\left.\begin{array}{l}5791\\5744\end{array}\right\}$ feeble.

IX.—Green.	X.—Green.	XI.—Green.
$\left.\begin{array}{l}5702\\5640\end{array}\right\}$ feeble.	$\left.\begin{array}{l}5576\\5509\end{array}\right\}$ very faint.	$\left.\begin{array}{l}5436\\5412\end{array}\right\}$ very faint.

The faint green bands are seen between $\lambda\lambda$ 5890 and 5086.

There are strong bands in the more refrangible rays between λ 4600 and λ 3600.

The lines are λ 4608.   Very strong.

4216.   Very feeble.

4078.   Very feeble.

Quantity of Strontium.

(2)   0·1 in 1 portion.

The spectrum is considerably weaker.   The bands in the green, violet, and ultra-violet extending to 3600 are very faint.

The lines λ 4216 and λ 4078 are extinct, but that at 4608 is strong.

(3) 0·01 gr.

The band at $\lambda\left\{\begin{array}{l}6878\\6782\end{array}\right\}$ is extinct.   The bands in the green and violet are absent.   The line λ 4608 is strong.

Quantity of Strontium.

(4) 0·001 gr.   The bands are changed in intensity and width : thus we have $\begin{Bmatrix} 6740 \\ 6550 \end{Bmatrix}$ very feeble.   By comparison with that of Hagenbach and Konen's spectrum it is observed that $\begin{Bmatrix} 6620 \\ 6520 \end{Bmatrix}$ fairly strong, must be included in the foregoing band, and $\begin{Bmatrix} 6500 \\ 6410 \end{Bmatrix}$ fairly strong, is split into two λ $\begin{Bmatrix} 6360 \\ 6310 \end{Bmatrix}$ feeble, $\begin{Bmatrix} 6115 \\ 6015 \end{Bmatrix}$ fairly strong.   The line λ 4608 is fairly strong.

(5) 0·0001 gr.   Three bands in the red are feeble :

$$\begin{Bmatrix} 6620 \\ 6520 \end{Bmatrix} \qquad \begin{Bmatrix} 6500 \\ 6410 \end{Bmatrix} \qquad \begin{Bmatrix} 6115 \\ 6015 \end{Bmatrix}$$

The line λ 4608 also appears faint.

(6) 0·00001 gr.   The line λ 4608 is very faint.   No bands.

STRONTIUM CHLORIDE.

Measurements of the bands more refrangible than λ 5890 in the flame spectrum of strontium chloride, in quantity equivalent to 0·5 gr. of strontium, compared with measurements made from the nitrate which gives the bands of the metal, and with C. M. Olmsted's measurements of corresponding bands.

Description of Spectrum.

	λ		λ	
	$\begin{Bmatrix} 5820 \\ 737 \end{Bmatrix}$ Faint.		$\begin{Bmatrix} 5838 \\ 812 \end{Bmatrix}$	Hartley, Roy. Soc. Phil.
	$\begin{Bmatrix} 698 \\ 630 \end{Bmatrix}$ Faint.		$\begin{Bmatrix} 791 \\ 744 \end{Bmatrix}$	Trans., 1894, vol. **185** ; and Roy. Soc. Pro- ceedings, 1907, vol. **79**,
	$\begin{Bmatrix} 565 \\ 496 \end{Bmatrix}$ Faint.		$\begin{Bmatrix} 702 \\ 640 \end{Bmatrix}$	p. 242.
Diffuse broad bands. Metal pro- bably undergoing oxidation. So-called "oxide bands."*	$\begin{Bmatrix} 436 \\ 358 \end{Bmatrix}$ Very faint.		$\begin{Bmatrix} 576 \\ 509 \end{Bmatrix}$	
	$\begin{Bmatrix} 333 \\ 280 \end{Bmatrix}$ Very faint.		$\begin{Bmatrix} 436 \\ 412 \end{Bmatrix}$	
	$\begin{Bmatrix} 214 \\ 161 \end{Bmatrix}$ Very faint.			
	$\begin{Bmatrix} 130 \\ 054 \end{Bmatrix}$ Very faint.			
	$\begin{Bmatrix} 031 \\ 4986 \end{Bmatrix}$ Very faint.			
	4608 An intensely strong line.			

* As with calcium and magnesium, these are metal bands, the metal undergoing oxidation.—Roy. Soc. Proc., vol. **79**, p. 242.   1907.

	λ		Olmsted. 1906.[*] λ
Bands well defined, sharp on both edges. Common to all haloid salts of strontium.	4579 566 }	Fairly strong.	4565·4
	557 542 }	Fairly strong.	545·82
	538 523 }	Fairly strong.	524·5
Bands degraded towards the red. Common to all haloid salts of strontium.	435 423 }	Strong.	421·4
	416 403 }	Strong.	400·38
	394 386 }	Faint.	384·0
	377 366 }	Strong.	362·1
	357 345 }	Strong.	341·3
	336 304 }	Very faint.	303·1
	297 282 }	Very strong.	281·4
Bands degraded towards the red. Strontium chloride bands.	4033 011 }	Very strong.	{ 4015·36 012·00
	003 3986 }	Very strong.	{ 008·86 3986·02
	979 958 }	Very strong.	961·85
	953 936 }	Very strong.	936·62
	932 917 }	Strong.	{ 931·2 918·9
Metal bands.	912 894 }	Faint.	{ 914·3 897·0
	887 875 }	Very faint.	
Diffuse broad bands. Metal bands.	3797 780 }	Very faint.	{ 797·6 783·0
	772 755 }	Very faint.	{ 779·3 776·0
	747 732 }	Very faint.	{ 743·5 735·5

Lecocq de Boisbaudran in "Spectres lumineux" gives beautiful drawings of the chloride spectra with maps of the wave-lengths of the bands, and a full description of them in the text.

BARIUM.

Barium nitrate $Ba(NO_3)_2$ was the salt used.

<table>
<tr><td>*Quantity of Barium.*</td><td>*Description of Spectrum.*</td></tr>
<tr><td>(1) 0·5 gr. in 5 portions.</td><td>A strong banded spectrum in the red, orange, green, and blue.</td></tr>
</table>

Quantity of Barium.

Description of Spectrum.

(1) 0·5 gr. in 5 portions.   A strong banded spectrum in the red, orange, green, and blue. Red $\begin{Bmatrix} 7318 \\ 6718 \end{Bmatrix}$ strong.   Feeble bands at λ 6530, 6320, and 6040. Between λ 6718 and 5536 there are several bands, composed of flutings with well-defined edges on the more refrangible side, described as composite bands.   Following these are four simple or diffuse bands in the green, which have the same intensity on both sides and are very strong.

$$\begin{array}{cccc} 5426\} & 5346\} & 5170\} & 4904\} \\ 5370\} & 5232\} & 5840\} & 4842\} \end{array}$$

A line λ 5536 is very strong.   A continuous spectrum extends very feebly to the violet.

(2) 0·1 gr. in 1 portion.   The spectrum is much weakened.   A number of the fine red bands have disappeared.   The broad diffuse bands have become narrower as well as more feeble.

(3) 0·01 gr.   The strong band commencing about λ 7000 and that commencing about λ 5080 are barely seen; all other bands have disappeared.   The line λ 5536 is still strong.

(4) 0·001 gr.   There are no bands, and the line λ 5536 has become very faint.

(5) 0·0001 gr.   No spectrum but the sodium line.

METALLIC SILVER.

Description of Spectrum.

Two groups of bands of different characters; in one, the bands are diffuse and degraded equally on either side.   This group lies between λ 4700 and λ 4300.

The second group is altogether different; it may be termed a composite band composed of a number of fine lines, degraded towards the red, the lines not only

being finer and feebler, but also more widely separated with increase of wave-length; it has a strong line at the head, λ 3383. A second very strong line λ 3280·8 is at the head of a second band, which is scarcely represented at all when 0·5 gr. of Ag is used.

All the lines and bands observed and recorded in this spectrum were measured.

Measurements of all the lines and bands observed in the spectrum.

Quantity of Silver.	λ	Lines.
0·5 gr.	7665·6	K, impurity line.
	6675	Very faint.
	6312	Ca, impurity. Faint band.
	6250⎱ 6146⎰	Ca, impurity. Faint band.
	5896·2⎱ 5890·2⎰	Na, impurity.
	5828⎱ 5806⎰	Ca, impurity. Faint band.
	5356	Tl ? *Very* faint.

Diffuse bands.

4699⎱ 4643⎰		*Very* faint.
4600⎱ 4594⎰		Faint band.
4574⎱ 4542⎰		Feeble.
4523⎱ 4493⎰		Feeble.
4476⎱ 4453⎰		Feeble.
4438⎱ 4418⎰		Feeble.
4407⎱ 4379⎰		Feeble.
4369⎱ 4346⎰		Very faint.
4342⎱ 4318⎰		Very faint.

Quantity of Silver.	λ	Diffuse bands.		
0·5 gr.	4305 ⎱ 4303 ⎰	Very faint.		
	4226·9	A strong line. Ca, impurity.		
	4047 ⎱ 4043 ⎰	Feeble line. ⎱ Strong line. ⎰	A pair. K, impurity.	
	3857	Very faint.		
	3772	Strong. Tl. ?		
	3741	Very faint.		
	3733	Very faint.		
	3716	Fairly strong.		
	3406·5 ⎫ 3401 ⎪ 3398 ⎬ 3395 ⎪ 3393 ⎭	A strong composite band.	⎧Faint. ⎪Faint. ⎨Faint. ⎪Faint. ⎩Faint.	
	3383	Very strong line.		
	3357	Very faint line.		
	3332	Faint.		
	3308	Faint.		
	3280·8	A very strong line.		

Remarks.—The series of diffuse bands lying between λ 4700 and λ 4300 is well seen with 0·5 gr. of silver.   The very strong line common to the arc and spark, λ 3383·0, is shown to be preceded by a strong composite band, the components of which are lines, or very narrow bands, but so far they have been resolved into merely very fine lines.   This composite band is extinct with 0·1 gr. of silver in the flame, but the diffuse bands still remain faintly visible.

Quantity of Silver.	*Description of Spectrum.*
0·1 gr.	The bands between wave-lengths 4700 and 4290 are well seen. Lines are broad and strong at wave-lengths 3383 and 3280·8.
0·01 gr.	No bands. The above lines are alone visible.
0·001 gr.	The same lines are shown decreasing in strength.
0·0001 gr.	The same lines are shown weak.
0·00001 gr.	Nothing visible.

Silver yields no banded spectrum unless there is more than 1 centigram of metal in the flame; and no spectrum at all unless there is more than $\frac{1}{100}$ of a milligram present.

The spectrum of calcium consisting of the red and green bands and the blue line, also the violet lines of potassium, all appear in these spectra, being strongest where there is 0·1 gr. Ag, diminishing in intensity down to 0·00001 gr., when they are hardly visible. These impurities appear to be caused by dust in the air.

Experiments were devised for the purpose of ascertaining whether the broad diffuse bands are a consequence of the vapour-pressure of the silver in the flame, or of its volume, *i.e.*, quantity merely. To this end 0·1 gr. was burnt in the flame on one paper, and 0·01 gr. on each of ten papers : the quantity of silver is the same in both cases; but the pressure is ten times as great in the former as it is in the latter. If the bands are emitted by the silver vapour, and are a consequence of the vibrations within the molecule, 0·1 gr., whether introduced all at once, or introduced very gradually, should make no difference in the spectrum. If the bands are caused by the translatory vibrations of the molecules, then, owing to their diminished freedom of motion when the vapour-pressure is increased, the bands should be visible when 0·1 gr. is introduced into the flame at one operation, but not when the spectrum results from the aggregate effect of ten times 0·01 gr., because in the latter case the molecules have greater freedom of motion. In the possible third event, where the effect is neither that of the actual quantity of silver used, nor simply that of vapour-pressure of the silver in the flame—in other words, where it cannot be supposed to be due to either a molecular motion or to an intramolecular motion—it must be caused by the large volume of the vapour at a considerable pressure, and may possibly be an absorption phenomenon, which can be imagined as being produced by a continuous spectrum between λ 4700 and λ 4290 being emitted by the great body of the vapour, and this having to traverse successive layers of vapour at different temperatures, and therefore of relatively different densities.

To determine this point, 0·5 gr. should be placed in the flame on one paper, or in one portion ; and also on five papers, or in five portions, each containing 0·1 gr. ; then under the latter conditions the bands should not be more numerous with five papers than with one, but they should be more intense. The results obtained, which appear to confirm this hypothesis, are as follows :—

Quantity of Silver.	*Description of Spectrum.*
0·1 gr. × 5.	Bands shown strongly as before. *See* p. 46.
0·1 gr.	Bands shown feebly but distinctly.
0·01 gr. × 10.	No bands but a continuous spectrum,* which is much stronger throughout than the previous spectrum. The two lines at 3383 and 3280·3 are both very strong.
0·01 gr.	No bands. The two lines are alone visible.

* Probably due to the filter-paper.

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These experiments appear to prove then, first, that the large volume of vapour at the atmospheric pressure is necessary to give rise to these particular bands.

An endeavour to repeat these experiments so as to gain further information concerning the composite bands, the heads of which are the lines λ 3383 and 3280·8, was rendered futile by experimental difficulties, arising from the large quantity of metal which it was necessary to volatilize at one operation before these bands could be developed. The results on this account could not be rendered strictly quantitative, because it was found necessary to maintain an excess of silver vapour in the flame, or to place more silver in the flame than could with certainty be vapourized. The most interesting fact in connexion with this group of elements is that narrow bands have been observed about the same positions, under similar conditions, in the spectra of the alkali metals. The manner in which photographs of the spectra showing these bands were obtained I have already described in the case of lithium, sodium, and potassium.* The foregoing account of the rubidium spectrum gives the position of the bands as lying between λ 5100 and 4400.

The following tabulated statement is useful for comparison :—

				λ		λ					At. mass.
Li,	.	.	.	4677	to	3610	Li,	.	.	.	7·03
Na,	.	.	.	4800	to	3600	Na,	.	.	.	23·05
K,	.	.	.	4800	to	3600	K,	.	.	.	39·15
Rb,	.	.	.	5100	to	4400	Rb,	.	.	.	85·5
Ag,	.	.	.	4700	to	4290	Ag,	.	.	.	107·93

With regard to the spectra of the alkali metals it was remarked (*loc. cit.*) that the bands are individually wider, and also wider apart, the larger the atomic mass of the element vapourized, which also means as the density of the vapour increases.

Silver has the highest vapour-density, and the bands in its spectrum are both wider and wider apart than those of the alkali metals; they are produced also with very great facility, probably because the silver vapour is not liable to oxidation, so that the only change it undergoes is solidification. The bands cannot be connected with the atomic weight of the metal excepting through its vapour-density.

The next element to be considered is copper. It has already been pointed out that it belongs to the group of metals with monatomic molecules. Its spectrum contains two sharp composite bands, and two diffuse bands, between which there is a close connexion. It will be seen also that the bands are almost the ultimate rays of this element. The quantitative results obtained from the copper spectrum lead

* "On the Thermo-Chemistry of Flame-Spectra at High Temperatures."—Proc. Roy. Soc., A., vol. **79**. 1907.

to no other conclusion than that the composite bands are the result of vibrations taking place within the molecule, and not to the vapour-pressure ; neither to the great volume of vapour, nor to the vapour-density of the molecule.

As the composite bands in the spectrum of silver are analogous to those of copper, and whereas it has been shown that silver cannot be submitted to the same crucial quantitative experiments, it may be very reasonably assumed that the similarly constituted bands in the spectrum of silver have a similar origin. This is the most probable explanation, because there are other bands in the spectrum of silver which have been shown by their behaviour to have a different origin, and one depending apparently upon the great density of the silver vapour.

[SILVER—*Description of Spectrum.*

SILVER.

Further measurements of lines and bands photographed from the oxyhydrogen flame spectrum of 0·5 gr. of metallic silver. Potassium and calcium, lines and bands, appear as impurities.

Description of Spectrum.

		λ		
	K.	7665·6		
Very faint.		6675		
Faint band.	Ca.	6312		
Faint band.	Ca.	{ 6250		
		{ 146	Bands in silver spectrum from "Flame-Spectra at	
	Na.	{ 5896·2	High Temperatures."—Roy. Soc. Phil. Trans.,	
		{ 890·2	vol. **185**, pp. 161–212. 1894.	
Faint band.	Ca.	{ 828		
		{ 806		
Very faint. Tl. ?		356	λ	
Very faint band.		4699 }	4696·0 }	
		643 }	650·8 }	
		600 }	616·5 }	
		594 }	591·0 }	
		574 }	563·4 }	
		542 }	533·4 }	
		523 }	519·0 }	
		493 }	490·9 }	
Faint band.		476 }	470·9 }	
		443 }	449·8 }	
		438 }	424·8 }	
		418 }	408·6 }	
		407 }	396·2 }	The bands are confused hereabouts, as
		379 }	373·5 }	if over-lapping occurred. — See
		369 }	360·7 }	Plate 7, Phil. Trans., vol. **185**.
		346 }	347·0 }	1894.
		342 }	330·9 }	
Very faint band.		318 }		
		305 }		
		303 }	300·5 }	
A strong line. Ca.		4226·9		
Faint line. } A pair. K.		4047		
Strong line. }		043		
Very faint line. } Tl. ?		{ 3857		
Strong line. }		{ 772	3775·2	
Very faint.		741		
Very faint.		733		
Fairly Strong.		716	712·7 ?	
		3406·5	407·0	
		401	401·0	
Faint. A composite band.		398	397·8	
		395	395·0	
		393	392·5	
A very strong line.		383	383·5	
A very faint line.		357	357·7	
Faint.		332	331·7	
Faint.		308	309·2	
A very strong line.		280·8	282·1	Centre only measured.

The series of bands between λλ 4700 and 4300 is well shown on the photograph. The silver lines λλ 3383 and 3280·8 are each at the head of a fine composite band consisting of a number of fine lines. On p. 167 of "Flame-Spectra at High Temperatures" I have described how these two lines correspond with two in the spark spectrum, their wave-lengths being 3382·6 and 3280·45 respectively (Hartley and Adeney), and how they appear as fine lines when the silver is diluted with some other metal and volatilized in the oxyhydrogen flame. This is shown on Plate 7 of the same publication in the spectrum of bismuth, and the lines have the same appearance when lead, copper, or other metals, ores, or minerals are examined in the same manner, if they contain traces of silver. This has been observed in some hundreds of substances. It will be easily understood from an inspection of the engraving (2 Silver) on Plate XXIX. of "Banded Flame Spectra of Metals,"* how impossible it is to obtain accurate measurements which are concordant when varying quantities of silver are volatilized, inasmuch as the lines become converted into bands which are developed more on the side of the less refrangible rays.

The same observation applies to band spectra in general; they are not under all conditions bounded by the same rays of definite wave-lengths, but vary in width and intensity with the conditions under which the substances from which they originate are vapourized.

The measurements quoted for comparison in the present communication were made from a much stronger spectrum than those taken from spectra representing weighed quantities of metal. The exposure of the photographic plate was longer also. It is also to be noted that the plates of Wratten and Wainwright used latterly are much more equally sensitive throughout the whole spectrum than any which could be obtained previously, so that lines as far down in the red as λ 7665·6 appear. This admirable quality also serves to modify the spectra.

The composite band is extinct when only 0·1 gr. of silver is present in the flame, but the diffuse bands are still faintly visible, and the two lines at the heads of the composite bands are also visible.

<div align="center">

COPPER.

The salt used was $Cu\,(NO_3)_2 \cdot H_2O$. *Photographed with Wratten and Wainwright's panchromatic plates.*

</div>

Quantity of Copper.	*Description of Spectrum.*
0·5 gr. in 5 portions.	A beautiful banded spectrum, extending from the yellow sodium lines into the blue. There are five series of bands—

(1) Between λ 5100 and λ 5800, a broad band of equal intensity on either side, but composed of a number of diffuse and very narrow bands. This band

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* Hartley and Ramage, Scient. Trans. Roy. Dublin Soc., 2, vol. vii., pp. 339–352. 1901.

differs in its constitution from the bands described below, in the more refrangible rays, as these are all degraded towards the red.

(2) A diffuse composite band lies between λ 5100 and 4700 less strong than the band (1), but composed of a number of fine narrow bands. These constituent bands are likewise diffuse, but are better defined than those in (1).

(3) A diffuse composite band lies between λ 4650 and 4279. This is a very strong band, composed of a great number of very fine lines, all of which are very sharp.

(4) Between λ 4279 and 4000 is a strong band, composed of a series of fine sharp lines degraded towards the red, and of diminished intensity as compared with (3). A sharp composite band.

(5) Between λ 4000 and 3800 is a similar band of fine lines, much fainter than (4). A sharp, composite band.

In addition to the bands the line λ 3274 also appears strong. The similar line belonging to this spectrum at λ 3248 falls just beyond the edge of the photographic plate, when the instrument, as in this case, is adjusted for photographing the extreme red rays.

Quantity of Copper.

0·1 gr.

The intensity of the whole spectrum is much reduced.

Bands.

(1) A diffuse composite band, fairly strong, between λ 5800 and 5100.

(2) A diffuse composite band between λ 5100 and 4700, feeble.

(3) A sharp composite band between λ 4650 and 4279, rather strong.

(4) A sharp composite band between λ 4279 and 4000, very feeble.

(5) The band between λ 4000 and 3800 is quite extinct.

Lines λ 3274 rather strong.

0·01 gr.

A very feeble spectrum throughout.

Bands.

Between λ 5800 and 5100, a feeble diffuse composite band.

Between λ 5100 and 4700, band extinct.

Between λ 4600 and 4279, a feeble sharp composite band.

Between λ 4279 and 4000 the band is extinct.

Line λ 3274 is feeble.

0·001 gr.   No bands. The line λ 3274 is just visible.

0·0001 gr.   Nothing visible.

NOTE. — A close connexion between the diffuse and sharp bands is an important feature of the copper spectrum. Thus, the diffuse composite band

between λ 5100 and λ 4700 disappears at the same time as the sharp composite bands between λ 4279 and λ 4000; likewise the strong diffuse composite band between λ 5800 and 5100 disappears along with the strong sharp composite band between λ 4650 and 4279. The line λ 3274 persists after the bands have disappeared.

Quantity of Copper.

0·1 gr., in 1 portion.

Bands.

Between λ 5800 and 5100, a diffuse composite band, fairly strong.
Between λ 5100 and 4700, a diffuse composite band, feeble.
Between λ 4650 and 4279, a sharp composite band, rather strong.
Between λ 4279 and 4000, a sharp composite band, feeble.
Line λ 3274, strong.

0·1 gr. in 10 portions of 0·01 gr.

The whole spectrum is more intense than the foregoing, and there are five bands instead of four. This is accounted for by there being the same quantity of copper in the flame, but introduced in ten small proportions, which increases the exposure of the photographic plate to an extent which is at least five times as long a period as that occupied in the previous case.

Bands.

Diffuse composite between λ 5800 and 5100, strong.
Diffuse composite between λ 5100 and 4700, rather strong.
Sharp composite between λ 4650 and 4279, strong.
A sharp composite band between λ 4279 and 4000, rather strong.
A sharp composite band between λ 4000 and 3800, very feeble.
Line λ 3274, very strong.

0·01 gr. in 1 portion.

Two bands.

Diffuse composite band between λ 5800 and 5100, very feeble.
Sharp composite band between λ 4650 and 4279, very feeble.
These are apparently near the point of extinction.
Line λ 3274, feeble.

0·01 gr. in 10 portions

This experiment and the previous one are comparable with 0·1 gr. in 1 portion, and in 10 portions respectively.

Bands.

A diffuse composite band between λ 5800 and 5100, feeble.
A diffuse composite band between λ 5100 and 4700, very faint.
A sharp composite band between λ 4650 and 4279, strong.
Line λ 3274, strong.

NOTE.—The spectrum 0·1 gr. in 1 portion has four bands—the two sharp composite and two diffuse composite corresponding; but the same quantity in

10 portions shows five bands—four being stronger than the foregoing.   Similarly, 0·01 gr. in 1 portion has two feeble bands, but the same quantity in 10 portions has three, that between λ 4650 and 4279 being a strong band.   This confirms the previous observations.   The sharp composite bands result from the vibrations within the molecules.

LEAD.

The salt used was lead acetate dissolved in water. $Pb (CH_3 \cdot COO)_2 \cdot 2H_2O$.

Quantity of Lead.	Description of Spectrum.
(1) 0·5 gr. in 1 portion.	The characteristic strong banded spectrum of lead. The bands which are degraded towards the red are fluted bands, extending the whole length of the spectrum, but they are strongest between λ 4900 and 4058. They are simple bands, that is to say, not composed of groups of lines. Lines λ 4058, 3682, 3639, all strong. The two silver lines λ 3388 and 3281 are also faintly visible, and are impurity lines.
(2) 0·1 gr.	Bands. Strong between λ 4900 and 4058. Lines. The three lead lines are all strong.
(3) 0·01 gr.	Bands. Between λ 4900 and 4058 are feeble.
(4) 0·001 gr.	No bands. Lines—The three lines are very feeble.
(5) 0·0001 gr.	The line λ 4058 is just visible.
(6) 0·00001 gr.	Nothing visible.
(1) 0·1 gr. in 1 portion.	Bands. Between λ 4900 and 4058 are strong. Lines. The three λ 4058, 3682, 3639 are strong.
(2) 0·1 gr. in 10 portions.	The spectrum is almost identical with the above, the difference being that the bands are somewhat more diffuse.
(3) 0·01 gr. in 1 portion.	No bands. The three lines are fairly strong.
(4) 0·01 gr. in 10 portions.	No bands, but a feeble continuous spectrum is visible between λ 4900 and 4058, where the bands are strongest in the foregoing spectra. The three lead lines appear strong.
(5) 0·001 gr.	The bands are extinct and the three lines feeble.

In spectrum (4), the feeble continuous rays visible between λ 4900 and 4058 are in all probability caused by the burning of the filter-papers, and if so are the spectrum of carbon monoxide.

Tin.

The salt used was crystallized stannous chloride $SnCl_2 \cdot 2H_2O$ dissolved in water.

Description of Spectrum.

Quantity of Tin.

(1) 1·0 gr. in 10 portions.   (Plate 7).—An intense banded spectrum, extending from $\lambda\,5000$ to the end of the photograph at $\lambda\,3250$.   The bands are flutings not composed of separate lines in groups, but having sharp edges. Lines, none.

(2) 0·5 gr. in 5 portions.   The bands are strong throughout.

(3) 0·25 gr. in 2 portions.   Strong bands throughout.

(4) 0·1 gr.   Bands feeble throughout.

(5) 0·01 gr.   Merest indication of bands between $\lambda\,4700$ and 3490.

(1) 0·1 gr. (Pl. 8).   Feeble bands throughout from $\lambda\,5000$ to 3250.

(2), (3), (4), (5) 0·01 gr., 0·001 gr., 0·001 gr., and 0·0001 gr.   No spectrum.

Here it will be observed that spectrum has entirely disappeared when the quantity of tin has been reduced to less than 1 centigramme; and that no lines appear, the spectrum being a banded one throughout.

Thallium.

The salt used was fused $TlNO_3$ dissolved in water.

Quantity of Thallium.

Description of Spectrum.

(1) 0·5 gr. in 5 portions.   No very distinct bands, but a continuous spectrum throughout, in which there appear rudimentary bands and lines.

Lines $\lambda\,5351$ and 3776, very strong.

A pair $\lambda\,\begin{Bmatrix} 3530 \\ 3519 \end{Bmatrix}$ fairly strong.   These are the heads of bands degraded on the less refrangible side.

(2) 0·1 gr.   A continuous spectrum cut off at λ 3530.

Lines λ 5351 and 3776, strong.

A pair λ $\begin{Bmatrix} 3530 \\ 3519 \end{Bmatrix}$ fairly strong.

(3) 0·01 gr.   Lines only. λ 5351 and 3776, fairly strong.   The pair above are feeble.

(4) 0·001 gr.   Lines λ 5351 and 3776 are moderately strong.   The pair λ $\begin{Bmatrix} 3530 \\ 3519 \end{Bmatrix}$ appear very feeble.

(5) 0·0001 gr.   The line λ 5351 is very faint; λ 3776 is fairly strong.

(6) 0·00001 gr.   The sole line visible, λ 3776, is very faint.

Here the ultimate line is at λ 3776, and the quantity necessary to produce it is $\frac{1}{100}$ of a milligramme of thallium.

The more recent quantitative experiments given here in detail were carried out by my assistant, Mr. A. G. G. Leonard, A.R.C.SC.I., during the past three years.

Summary of the Observations on the Alkaline Earth-Metal Spectra.

CALCIUM.

The spectrum of the metal in the Bunsen or Mecke burner flame.

With large quantities, there are four intense bands, one intense line, and three very feeble. The lines are identical with those in the spark spectrum, λλ 4226·9, 4586, 4455, and 4435.

With small quantities of calcium there are bands only.

The flame spectrum of calcium, as obtained from its compounds, with the Mecke, or Mecke blast-burner.

Bands only are observed.

The same compounds, heated in the oxyhydrogen blow-pipe flame.

With a large quantity of substance, the spectrum consists of seven very strong bands, one intense line, and four comparatively feeble lines. The five lines are identical with the strongest lines in the arc and spark spectra of the metal.

The spectrum of the uncondensed spark passing between electrodes of metallic calcium in air, *in vacuo*, and in hydrogen, at normal and reduced pressures.

The spark is intermittent and variable, and, in hydrogen, at normal and reduced pressures, very irregular, intermittent, and uncertain.*

The spectrum, under all these conditions, consists both of bands and lines.

The spectrum of the uncondensed spark passing from solutions of calcium salts.

The spectrum consists of bands only, the less refrangible edges of which become reduced to short lines with diminishing quantities of substance. λ 4226·9 also appears.

The spectrum from a condensed spark passing between metallic electrodes.

Very feeble bands, with very strong and numerous lines. The characteristic spark spectrum.

The same, taken from solutions of calcium salts.

Very feeble bands, with strong lines as above.

In the above series of spectra we see the gradual development of a line spectrum from a band spectrum. The line which first makes its appearance may be supposed to be the fundamental vibration of the element, and its wave-length is 4226·9. It is the last to disappear, and may be termed, following M. A. de Gramont, the *ultimate line*. Next in importance are the red and green bands, which have a persistency almost equal to that of the ultimate line. But the most interesting fact is the production of band and line spectra simultaneously from the compounds of calcium in the oxyhydrogen flame, the lines of which belong to the same series as those produced by the condensed spark and the arc, but with less intensity. Here are rendered visible the conditions which obtain in the dissociation of compounds at different temperatures; but that we are dealing with an element is evident; first, because the lines belong to a series for which a formula has been established in which the atomic weight is a function; secondly, the intense band-spectrum and the series of lines are obtainable direct from the element itself when vapourized in the flame; thirdly, seven strong bands, and five of the strongest lines observed in the arc and spark spectra, are simultaneously obtained from calcium compounds when heated in the oxyhydrogen flame.

The compounds of strontium and barium yield similar results, but the number and variety of the different spectra examined have not been so great. Nevertheless it has been proved† that in these instances the spectra obtained are the spectra of

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* " Note on the Spectra of Calcium and Magnesium as observed under different conditions."—Scient. Proc. Roy. Dublin Soc., vol. xi. (N.S.), p. 243. 1907.

† "On the Thermo-Chemistry of Flame-Spectra at High Temperatures."—Proc. Roy. Soc., A, vol. 79, pp. 242–261. 1907.

the elementary substances when oxysalts only were used.   Chlorides in large quantity yield chloride bands along with bands obtained from the oxides, but which are the bands of the metals, though possibly undergoing combustion.

The banded Flame-Spectra of Beryllium, Magnesium, Zinc, and Cadmium.

These were previously investigated by Hartley and Ramage.*   The banded spectra were not so easily obtained as those of alkaline earth group; but it was a very notable feature in the spectra of magnesium, zinc, and cadmium, that lines common to the arc and spark accompanied the bands.   A retrospect of these is given.

MAGNESIUM.

Banded Flame-Spectrum.

Lines.
λ

5184 ⎫
5174 ⎬ A triplet common to flame, arc, and spark.
5178 ⎭
4572   A line common to flame, arc, and spark.

ZINC.

Banded Flame-Spectrum.

Lines. λ		Corresponding Spark-lines. λ
4811 ⎫		Kirchhof, . . . 4810·1
4723 ⎬ A triplet.		Exner & Haschek, . . 4722·37
4680 ⎭		Exner & Haschek, . . 4680·4
4259 ⎫	Three lines, components of a band;	
4255 ⎬	a close group ; similar to three in	
4250 ⎭	cadmium.	
4197	Components of a band.	Exner & Haschek, . . 4195.7

CADMIUM.

Banded Flame-Spectrum.

Lines. λ		Corresponding Arc-lines. λ
5086 ⎫		Kayser & Runge, . . ⎧ 5086·1
4800 ⎬ A triplet.		Reversed arc lines, . . ⎨ 4800·1
4678 ⎭		Eder & Valenta. Spark, . ⎩ 4678·4
4417 ⎫		Exner & Haschek. Spark, 4415·7
4411 ⎬		Eder & Valenta, „ 4413·2
4404 ⎭		Eder & Valenta, „ 4403·5
		Kayser & Runge observed 4413·5 in the arc.
4294	Components of a band.	Eder & Valenta, . . 4293·9
4215		„ „ . . 4214·0
4179		„ „ . . 4177·5
4126		„ „ . . 4127·1
4076		„ „ . . 4075·8
4058		„ „ . . 4057·5
4034		„ „ . . 4035·1
4032		„ „ . . 4030·0
4008		„ „ . . 4009·2

* Scient. Trans. Roy. Dublin Soc.

Though the constitution of these banded spectra is very different from that of the calcium group of metals, yet the connexion between the band and line spectra of each element is a very intimate one, inasmuch as the lines appear to be developed from the bands. This is more particularly observable in the case of the most volatile metal of the group, cadmium. No such connexion is to be traced in beryllium, aluminium, and lanthanum band spectra, partly because of the difficulty in reducing their oxides, and in part because of their high boiling points.

The Tetrad Elements.

The banded spectra of tin and lead which belong to this group are of quite a different constitution from those belonging to any of the foregoing elements. They are fluted or channelled spectra.

There is a difference in behaviour in the two elements, probably due to a difference in their boiling points, that of tin being the higher.

Tin.

The banded spectrum of tin extended the whole length of the plate from λ 5000 to λ 3250. The bands have sharp edges, but no lines are visible, and by reducing the quantity of substance in the flame the bands become feeble throughout, and are finally extinct when the quantity of substance is reduced to less than 1 centigramme.

Lead.

The fluted bands degraded towards the red extend the whole length of the spectrum, but are strongest between λ 4900 and λ 4058. These bands are accompanied by three lines, $\lambda\lambda$ 4058, 3682, and 3639, all strong.

On reducing the quantity of substance in the flame, the lines survive after the bands are extinct. The ultimate line is at λ 4058, and is caused by $\frac{1}{10}$ of a milligramme of lead. The last appearance of the bands is caused by 1 centigramme of the metal.

On the Origin of different Bands.

There are bands in the spectra of the elements which have their origin in three conditions of matter in the flame. First, there are those which are without any sharp outline, ill-defined, or diffuse. The most pronounced are the bands in the flame spectrum of silver, in the blue region, and the bands in the spectra of the alkali metals. They are photographed only when large volumes of vapour

are in the flame; they are wider apart, and individual bands are wider, as the vapour-densities of these elements are greater. They do not shift appreciably in relation to their atomic weights towards the red or less refrangible rays, and probably therefore have not an atomic or molecular origin. It appears as if they originate from the mass of vapour in the flame, and are dependent apparently also on the vapour-pressure. The exact cause of the bands has not yet been definitely ascertained, but they are being submitted to a more searching examination. That they do not arise from the atomic constitution of the vapours is, I think, shown by a somewhat similar group of bands being photographed from the flame produced when ether-vapour mixed with hydrogen is burnt in the oxyhydrogen blow-pipe.*

†Second.—There are diffuse bands degraded on one side, but sharp and intense on the other. Such a band has been photographed in the red rays of potassium, but as a rule it is too feeble to show this distinctive character. There are also bands which extend on either side of a line, such as the broadening of the red line of lithium, and the yellow lines of sodium. These also depend on the volume of vapour in the flame.

Third.—Bands of a very definite character, such as those of calcium, strontium, and barium, not always degraded on one side or the other. These bands contain rays that are more intense than those on either side of them, and have the appearance of lines not well defined. They become intensified, sharper, and narrower by supplying the flame with hydrochloric acid; and, by the action of the spark, lines are developed from them. The bands become broadened and intensified by increasing the quantity of the element in the flame.‡

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* The photograph showing these bands is at present in the Franco-British Exhibition.

† With reference to the bands in the blue in the spectrum of silver, the conditions under which they have recently been photographed seemed to render it possible that they are due to interference; but as they were photographed in 1890 by a method which excludes this possibility, and yet renders the band sharper and more distinct, such a view is untenable. In a friendly communication for which I am indebted to Professor E. T. Whittaker, F.R.S., the opinion was expressed that instead of interference it might be possible to suggest "absorption, resonance, and mutual interaction of vibrating systems." In connexion with this subject, a publication by Professor R. W. Wood has recently appeared on Resonance Spectra of Sodium Vapour (*Phil. Mag.*, 1908 [vi], **15**, 581–601), in which an extremely complicated absorption spectrum has been described, showing about 6000 lines in the bluish-green. When illuminated by white light, the vapour becomes fluorescent, and gives an emission spectrum which is an exact counterpart of the absorption spectrum. From this it would appear probable that very small layers of vapour of the alkali metals would suffice to give some of these bands, due to absorption or to resonance, since the vapour is brilliantly illuminated by white light; but absorption could not be applied to the appearance of similar bands when nothing but ether vapour is burnt in the flame.

‡ Compare Spectra 1, 2, and 3 of fig. 1, and Nos. 1, 2, 3, 4, 5, and 6 of fig 2, Plate xx. Scient. Proc. Roy. Dublin Soc., vol. xi. (N.S.), p. 237, 1907.

Fourth.—Channelled or fluted band-spectra, such as those of tin, lead, antimony, and bismuth, extending through a wide range if not throughout the whole of the flame-spectrum. These appear to be quite independent of lines and unconnected with them. They are beyond all question the spectra of the elements. The banded spectrum of metallic manganese may also be classed with them.

Fifth.—Bands composed of lines, spaced with regularity, and grouped in a different manner, according to the nature of the element. The spectra of each group of metals in the periodic system are similarly constituted, as, for instance, those of zinc and cadmium, and those of copper, silver, and gold. There is an intimate connexion between these bands and the arc and spark lines of the same elements. The band-spectra are the spectra of the molecules of the elements, and the molecules have been well ascertained to consist of only one atom.

Sixth.—There are spectra composed chiefly of lines, whether the flame or the spark be employed, but which show diffuse bands of continuous rays, in some cases ill-defined, as, for instance, iron. Thallium, palladium, and iridium are examples* which may be classed with iron, though the two last have very definite composite bands.

In the spectra of the calcium group, the characteristic bands from which lines are developed by physical and chemical means are apparently caused by the act of oxidation of metallic vapour in the flame which had already been reduced from the oxide. The same may be said of the diffuse bands in the green which are observed in the spectrum of copper.

It is necessary to mention here some experiments on calcium which afford evidence in support of this view. When the spark without condenser is taken from metallic calcium in air and in hydrogen, and from a solution of calcium nitrate under the same conditions, the spectra are practically identical with the flame-spectrum of metallic calcium, with the oxyhydrogen flame-spectrum of calcium carbonate, and with calcium oxide in the Mecke burner. The red and green bands have lines in them which appear only as intense narrow radiations, but without differentiation of lines; they are placed rather towards the more refrangible side of the red band, and are situated in the midst of the green band, but they are neither well-defined nor sharp; also, the sodium lines, as seen in the same spectra, are rather diffuse; but when the air in the tube is changed for hydrogen, whether the spark be taken from the metal or from the salt, three beautifully distinct fine lines are observed in the red band, and two in the green band. Simultaneously the yellow sodium lines become not only very

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* Hartley and Ramage: "Banded Flame-Spectra of Metals."—Scient. Trans. Roy. Dublin Soc.

distinct and fine, but there appears a sharply defined dark space between them.

A survey of the facts shows that we have bands of different characters, which are to be assigned to the mass, the atom, and the molecule, respectively, of the different elements. The question as to the complexity of the molecules of many of the metallic elements has been studied by Tammann,[*] who concluded, from observations on the freezing points of metals dissolved in mercury, that even at low temperatures nearly all metals have monatomic molecules. Heycock and Neville[†] concluded that at high temperatures also copper, silver, gold, and lead have molecules which are monatomic. In a series of elaborate experiments H. von Wartenberg[‡] has determined the vapour densities at very high temperatures, and calculated therefrom the average molecular weights of a number of metals and non-metallic elements. For instance, silver at 2000° C. has a vapour density which proves the molecule to be monatomic.[§]

The temperatures measured do not exceed that which is obtained in the oxyhydrogen blow-pipe flame.

The following table gives some of von Wartenberg's determinations:—

Element.				Atomic Weight.	Average Molecular Weight.	Temperature.
Antimony,	.	.	.	120·2	128	2070° C.
Bismuth,	.	.	.	208	224	2070°
Zinc,	.	.	.	65·4	72	1200° to 2070°
Lead,	.	.	.	206·9	225	1600° to 1870°
Thallium,	.	.	.	204·1	220	1320° to 1690°

The boiling points of the following metals are given:—Thallium, 1280° C.; Lead, 1580°; Silver, 2050° to 2100°.

Copper, gold, magnesium, aluminium, and tin all boil at temperatures above 2200°.

The temperature of the oxyhydrogen blow-pipe is such that considerable quantities of silver can be placed in rapid ebullition and distilled, this being the method by which Stas obtained pure silver, and by which the banded flame spectrum of the metal was first photographed.[‖] Gold, copper, and tin, though very freely vapourized by the same means from considerable quantities of the metal, cannot with certainty be made to boil, though tobacco-pipes may be gilded in a few minutes by the condensation upon them of the gold vapour. Lead is so

* Zeit. f. physik. Chemie, 1882, **3**, p. 441.   ‡ Zeits. Anorgan. Chemie, 1907, **56**, pp. 320–336.
† Phil. Trans., **189**, A, p. 25. 1897.   § Metallurgie, 1906, **39**, p. 381.
‖ Hartley: "Flame-Spectra at High Temperatures."—Scient. Trans. Roy. Dublin Soc.

easily boiled away that by the analysis of minerals containing much lead there is danger to the operator of lead-poisoning, if the work is conducted in a closed photographic room. A similar risk from poisonous fumes is incurred when photographing the spectrum from metallic thallium. These facts are cited in order to show that the temperatures at which the banded spectra of lead, silver, cadmium, and thallium were obtained must have been considerably in excess of the boiling points of these metals; from which it may be inferred that the similarly constituted spectra of antimony, bismuth, tin, zinc, copper, and gold were photographed under similar conditions as to temperature, because the quantity of material in the flame in each case being smaller, the available heat for vapourizing it was in consequence greater.

The following discussion is restricted, as far as possible, to the chemistry of the subject, and, therefore, no reference is made to the beautiful theory of J. J. Thomson,[*] "On the Structure of the Atom," nor to the equally interesting paper, "Kinetic of a System of Particles illustrating the Line and Band Spectrum,"[†] by H. Nagoaka, although neither the facts in detail nor the views explained appear to be inconsistent with these physical theories, which account in a remarkable manner for homology in spectra and periodicity in the properties of the elements.

On the Relation of the Line to the Band-Spectrum of the same Element.

It has been shown that in the arc under different conditions, the bands of compounds such as chlorides,[‡] the bands of elements,[§] the arc lines, and the spark lines[||] of the elements may be obtained. Plücker and Hittorf[¶] believed that the bands and lines belong to allotropic modification of the same element, the allotropy depending solely on temperature. Allotropy is now known to be caused by either a loss of energy, as when amorphous carbon becomes successively graphite and diamond, or by a gain of energy, as when oxygen becomes ozone; in such instances the molecules undergo a change in constitution, but allotropy is unknown in a monatomic molecule in the gaseous state.

The view expressed by Kayser[**] is, when an element shows two spectra, one of lines corresponding to the atom, the other of bands, there is probably in the latter case a more complicated structure, an aggregation of atoms, or a molecule. We cannot even assume this to be the case when we know the vapour-densities of the

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[*] Phil. Mag. (6), vol. **7**, p. 237, 1904.   [†] *Ibid.*, p. 445. 1904.

[‡] Hagenbach.   [§] Plücker and Hittorf, Basquin, Liveing and Dewar, Hartley.

[||] Ch. Fabry and H. Buisson, C. R., vol. cxlvi., April 6th, 1908—"Presence of Spark-lines in the Arc-Spectra of Iron, Nickel, and Cobalt.

[¶] Phil. Trans., **155**, pp. 1–29, 1865.   [**] Kayser's "Handbuch der Spectroscopie," vol. ii., p. 258.

elements, and it does not appear to be consistent with the usual conception of the molecule of those substances which contain only one atom ; but it becomes quite intelligible if the view of the composite nature of the atoms be entertained, for the band-spectra belong to the elementary atoms, and may be considered as being caused by the vibrations, not only of the atoms themselves, but also of the component parts within the atom.   The facts adduced with regard to the spectrum of silver and of copper, I believe must be regarded as a proof of this.

I conclude, therefore, that *the banded flame-spectra of lead, antimony, bismuth, tin, zinc, cadmium, copper, silver, and gold are the spectra of the atoms.*

What relation, then, have the lines of the elements to the bands ?   It must be admitted that the lines are also the spectra of the atoms, and it may be inferred therefrom that component parts of the atoms are in a state of dissociation.   There is, however, an alternative view, which is based upon a somewhat different interpretation of the facts.   It is unquestionable that the arc and spark lines are caused by the operation of a largely increased amount of energy over that available in the flame, and by assuming that this excess is in part added to the material atom, it is conceivable that the components of the atom are thrown into a different mode of vibration, which increases their radiant energy, and so renders smaller quantities of matter recognizable, either by the brilliancy of their spectra, or by the intensity of their chemical action on a photographic plate.   The acceptance of this view so far would naturally lead one to expect that in the periodic system different groups of elements, according to their chemical properties, would acquire different quantities of energy, and individual elements belonging to the same group would show gradational differences in this respect.   The evidence of this would be that different groups would exhibit line-spectra with greater or less facility ; and elements of the same group, under the influence of the same source of energy, would differ in the number of lines of their spectra, or in the proportion of lines to bands.   Now, these conditions are exactly in accordance with observed phenomena, in forty at least out of forty-four elements.   To facilitate reference to them, the characteristic flame-spectra of the elements have been tabulated, but for particulars regarding the different spectra, the reader must consult " Flame-Spectra at High Temperatures " * and the " Banded Flame-Spectra of Metals."†

* Hartley, Phil. Trans. 1894, vol. **185**, Part. I., pp. 161–212 ; Parts II. and III., pp. 1029–1091.

† Hartley and Ramage, Scient. Proc. Roy. Dublin Soc., 1901, vol. vii., pp. 339–352.

The Characteristic Flame-Spectra of the Elements.

GROUP									SUB-GROUP
I.	Li,	K,	Rb,	Cs,	Na,	Cu,	Ag,	Au,	I.

Line spectra with greatest facility.   Banded spectra, with ultimate lines in Cu and Ag.

| II. | Be, | Ca, | Sr, | Ba, | Mg, | Zn, | Cd, | II. |

Band spectra, with limited line spectra.   Band spectra, with lines increasing in number with atomic weight.

| III. | B, | Sc, | Yt, | La, | Al, | Ga, | In, | Tl, | III. |

No spectra.   Band spectra.   Lines chiefly ; bands ill-defined.

| IV. | C, | Ti, | Zr, | Ce, | Si, | Ge, | Sn, | Pb, | IV. |

No spectra in this group.   Band spectra, with few lines in Ge and Pb.

| V. | N, | V, | Nb, | Di, | Ta, | (P, As), | Sb, | Bi, | V. |

No spectra in this group.   Band spectra.

| VI. | O, | Cr, | Mo, | W, | Ur, | S, | (Se), | Te, | VI. |

Chiefly No spectra.   Band spectra.   Se not examined.
lines.

Mn,   Bands very numerous and strong, with the ultimate lines

Fe, Ni, Co, } Line spectra, with bands of diffuse and indistinct character in the iron group. The lines
Pd,   Ir, } preponderating largely over the bands in both groups.

The following facts are to be observed :—

1st. The facility with which the alkali metals yield line spectra.

2nd. The facility with which the alkaline earth metals yield band spectra of a special character, and but few lines.

3rd. That the elements in groups* III, IV, V, and VI exhibited scarcely any but continuous spectra in the flame, nevertheless the corresponding arc and spark spectra are remarkable for their complexity.

4th. Each of the sub-groups contains, as a rule, three elements, which yield characteristic flame spectra, with either lines or bands preponderating.

* It is worthy of remark that the spectra of scandium and yttrium obtained with the condensed spark are similar in character, in that each element displays a beautiful group of bands. These are similar to the bands of beryllium and aluminium obtained with difficulty in the flame. Such bands are quite exceptional in spectra obtained from a powerful spark. The scandium and yttrium spectra display also at the same time a large number of lines.

In the absence of any positive proof of the dissociation of the atom, and the proof that highly endothermic reactions take * place between reacting substances in the oxyhydrogen flame, which are not accomplished by heat alone, and are therefore the result of an exalted chemical activity of the reacting substance, I conclude *that the metallic elements with monatomic molecules which exhibit two spectra, one of lines and the other of bands, can exist in two different conditions, the difference being in the larger amount of energy associated with the atom which exhibits a line spectrum. The acquisition of energy by the primitive or normal atom arises from its chemical properties, and from the excess of energy transferred to it in the flame, or arc, over that which is necessary to liberate the atom from its compounds.*

NOTE ON THE ILLUSTRATIONS.

The figures above the photographs give an approximate scale of wave-lengths. The two yellow sodium lines are indicated by the symbol Na, the mean of their wave-lengths being 5893. The number 6000 is at a little to the left of this. The number 3000 represents a wave-length lying just beyond the edge of the photograph.

On Plate I. the ultimate line in the spectrum of silver is shown as lying between 3500 and 3000. It is the least refrangible of the two lines that remain after the composite bands in which they occur have become extinct.

The figures in brackets after the name of the metal serve to identify the photographic plate from which the spectra were copied.

In one or two instances the description in the text may not exactly tally with the reproduction. On Plate II., for example, some lines are absent from the weaker spectra which are plainly visible on the silver prints from the same negative.

In the spectra of rubidium, cæsium, and thallium, it will be observed that in each case where there is a pair of lines, it is the more refrangible of the two which is the stronger, and which remains after the other has become extinct.

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* "On the Thermo-Chemistry of Flame-Spectra at High Temperatures."—Proc. Roy. Soc., A, **79**, pp. 242–261. 1907. See Part III., pp. 253–261.

Plate 1.
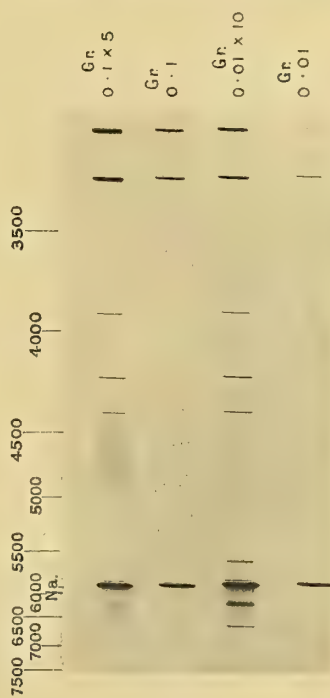
SILVER. (2)
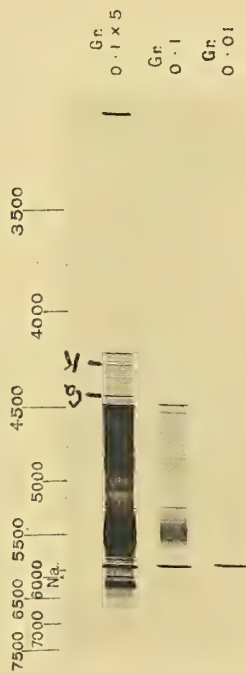
COPPER. (3)

COPPER. (4)
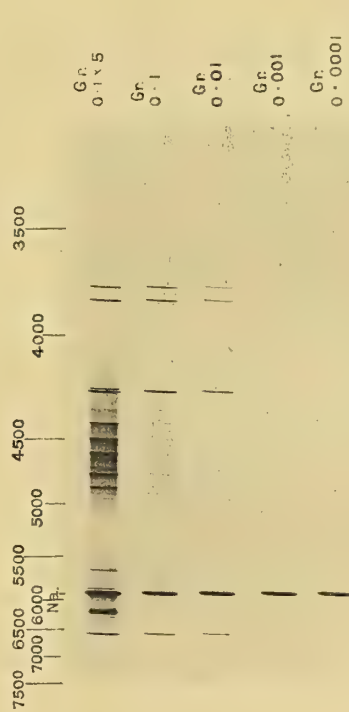
LEAD. (5)
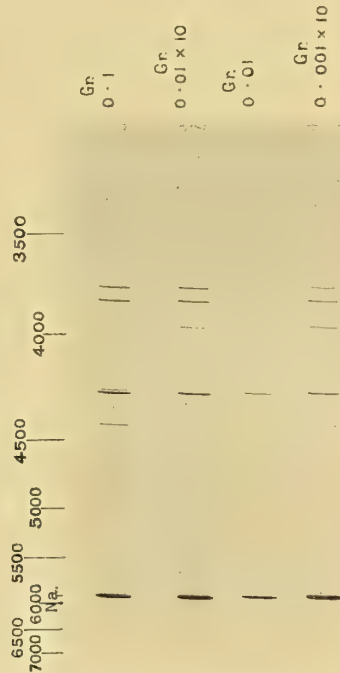
LEAD. (6)
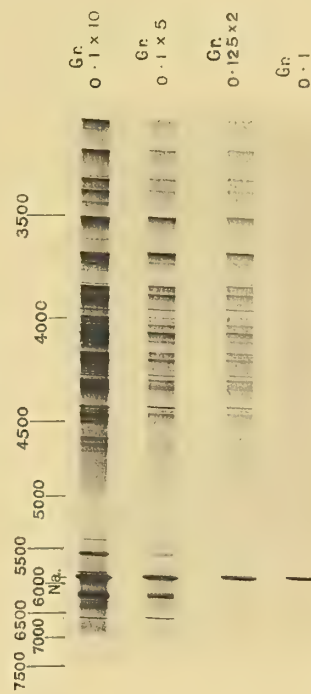
TIN. (7)

W. N. Hartley

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Plate II.

RUBIDIUM. (18)

CÆSIUM. (19)

THALLIUM. (9)
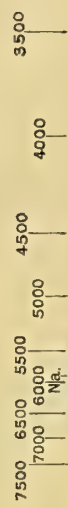
CALCIUM. (24)

STRONTIUM.

BARIUM. (25)

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TRANSACTIONS (SERIES II.).

VOLUME IX.

THE

SCIENTIFIC TRANSACTIONS

OF THE

ROYAL DUBLIN SOCIETY.

VOLUME IX.—(SERIES II.)

VIII.

THE ERUPTION OF VESUVIUS IN APRIL, 1906.

BY

H. J. JOHNSTON-LAVIS, M.D., D.Ch., F.G.S., ETC.,

Late Professor of Vulcanology in the Royal University of Naples.

(PLATES III.–XXIII., INCLUDING TWO MAPS.)

[COMMUNICATED BY PROF. GRENVILLE A. J. COLE, M.R.I.A., F.G.S.]

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State of Vesuvius anterior to the New Eruption.

WE find that several severe paroxysms shook the flanks of the great Neapolitan volcano during the nineteenth century, rivalling those of the preceding one. The most important of these paroxysms occurred in the years 1822, 1834, 1850, 1855, 1858, 1861, and 1872, besides which a considerable number of minor ones are recorded. The last important outburst preceding the one that we are about to consider was that of 1872, when extensive outpourings of lava took place, and a crater of some considerable size truncated the summit of the great cone.

After a period of a year and nine months, in January, 1874, the volcano showed signs of revival of its exhausted energy after the great outburst. From thence onwards, Vesuvius continued to exhibit constant activity, though little replenishing of the crater seems to have started before 1876. Eruptive cone-building seems then to have gone on with some regularity, increasing the filling up of the 1872 crater, and helped by the frequent overflow of lava into the annulus between the cone of eruption and the old crater. In October, 1878, the lava began to overflow the lowest lip of the old crater edge and down the cone into the Atrio. In September, 1879, when I first made acquaintance with Vesuvius, most of the northern and much of the eastern and western crater-lips of 1872 were already overlapped by new lava, and a considerable lava-plain filled the old crater. Near the centre of this crater-plain of lava rose a rapidly growing cone of eruption. About 1880 this eruptive cone began to overtop

the level of the south-west edge of the 1872 crater-rim, and thus added to the mountain's height.

During the next ten years small eruptions, accompanied by outpourings of lava, first from one side and then from the other, gutted from time to time the cones of eruption, which were again rapidly repaired. Frequently, several concentric crater-rings thus came into existence—on one occasion five such were figured and described by me. During this period some thirty-seven papers, articles, reports, etc., of mine record the changes at Vesuvius from 1879 onwards, a list of which is published in the Bibliography of Vesuvius in my " South Italian Volcanoes " (Furchheim : Naples, 1891). Two periods in this decade are interesting, as, although no very spasmodic or violent action was displayed, two large lava buttresses were constructed on the sides of the cone, constituting marked features in the outline of the mountain. These two buttresses also had, I believe, a marked influence in determining in part the point of overflow of two of the lava-streams of April, 1906. Early in 1883 lava reached the surface of the great cone in a S. E. azimuth, and continued to flow in small quantities, often not reaching the Pedimentina. This dribbling may be compared to the guttering of a stearine candle when the grease flows first in a straight line, until by cooling it directs the further flow first to one side and then to the other, building up gradually a buttress that forms an important addition to the original mass. This lava-mass eventually developed into a bulky hump on the slope of the great cone of Vesuvius facing Torre Annunziata. (Fig. 10, Pl. X., right side.)

Early in May, 1885, the great cone was again split down about one-third of its height, on the S. S. W. azimuth, and a repetition of the same buttress-building took place as in 1883. It was in this eruption that I first discovered hollow dykes, and was able to study the mechanism of their formation.* These two humps on the back of Vesuvius are well seen in the photograph. (Fig. 10, Pl. X., left side.) They limited the space of soft fragmentary material afterwards utilized by the zigzag path to Vesuvius, made by Sig. Fiorenza, and now destroyed by the last outburst.

I have referred to these masses, as probably their size and cohesiveness prevented the outbursts of lava of the 4th April from reaching the surface at a higher level, as the cone had there a considerable crust of the 1885 lava, so that the new fluid rock had to find its way out, probably obliquely and farther to the south than would have been determined by the true azimuth of the dyke, were it not for this obstruction. It is probably in great part due to this arrangement that the large subsequent slipping occurred on the south slopes of the great cone, owing to the struggle of the lava to reach the point of least

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* H. J. J.-L.—" L'Eruzione del Vesuvio nel 2 Maggio, 1885."—Ann. d. Accad, O. Costa d. Asp. Naturalisti, Era 3, Vol. i., Napoli. 1886. Illust,

resistance. The lava was, in fact, obliged to take a crooked course, and so in part disintegrated the cone at this unsupported spot.

In like manner, the great thick buttress on the south-east slope of the Vesuvian cone very likely prevented the radial dyke from reaching the surface beneath it, or the thick lava masses on the Pedimentina farther down. The fluid rock no doubt found the direction of least resistance in the old incoherent materials at a lower level, 600 metres, at the Bosco dei Cognoli, on the still only partially covered flanks of the prehistoric Monte Somma.

During the next few years, the height of the mountain steadily rose by additions of lava and scoria, on the lava-plain of what remained of the 1872 crater. Fluid rock in small quantities issued high up on different sides of the great cone; and when the magma-level in the chimney fell, owing to one of these lateral drains, some of the cone of eruption crumbled in, but was soon again repaired and added to.

On June 7th, 1891, the whole north side of the great cone was rent from the top down to the Atrio—that is 300 metres. Lava issued in fountains on the floor of the Atrio, inundating many hundreds of square metres of the almost level plain. Dr. L. Sambon, who was then my assistant, and myself, were nearly overwhelmed; but we escaped and clambered up the face of the Somma escarpment, and witnessed during the rest of the night one of the finest spectacles one could be present at with any chance of safety. This outflow continued with hardly any intermission till February, 1894. The rift in the side of the great cone became sealed up on the surface from the first days of the 1891 outburst, and a sort of permanent canal was established at its lower extremity, by which the lava issued during all these three years. The exit of this drain was at the base of the great cone in the Atrio.*

The flow was slow, so that by the cooling it soon raised the level of exit in that direction, and had to find a new path in another one; thus, by the constant increasing height of obstructing cooled lava at different points, the level of exit was raised by the growing pile of consolidated rock around it. The result of this was that a great lava-cone was built up in the Atrio, in which fragmentary ejecta took no part, and the summit of which stood away from the great Vesuvian cone. The apex of this lava-cone, now known as the Colle Margherita, was just short of 100 metres above the original point of lava issue that laid down its foundations three years before. The Colle Margherita slopes away in all directions, as sometimes the lava flowed far along the Atrio (3,000 metres maximum), which has been to a considerable extent filled up. In 1894 the deep notch in the outline of Somma and Vesuvius, so well known in the view

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* It is not unlikely that one of the hollow dykes (fig. B, p. 185) may have been the feeder of this issue of lava.

2 A 2

from Naples, was in part replaced by a third lower summit rising between the two.

From February, 1894, to July 3rd, 1895, most of the volcanic energy was displayed in adding to the cone of eruption and repair of the mountain-summit. On the latter date and the following days a radial rift, or, more likely several parallel ones, split the great cone from summit to base in a W. N. W. direction. The azimuth seems to have been bent near the toe of the great cone, and then to have assumed a due east and west direction. The rift reached the surface at several spots, giving rise to fumaroles at higher levels and lava-flows at lower ones, about midway between the base of the great cone and the end of the remnant of a ridge of Monte Somma, known as the Crocelli.

A permanent issue was established for the lava towards the surface-termination of the principal of these fissures ; and from this for four years, almost without intermission, the same process went on as at Colle Margherita. At the end of this time an imposing lava cone had grown up nearly 150 m. in height, forming a marked feature on Vesuvius, and completely blocking out the view of the Atrio from the Observatory, and hiding a good portion of the cone. In September, 1899, the last issue of lava took place, adding the final touches to a striking monument of mountain-building in the magnificent and imposing lava-cone now known as the Colle Umberto.

For about the next four years volcanic activity was chiefly displayed at the top of Vesuvius, cone and small crater succeeding each other continuously, but all uniting to raise the summit to a higher level. In the middle of March, 1903, increased activity was visible, and the mountain was in a markedly agitated state. With some variations this continued till July, when some streams of lava flowed down on the south slope of the great cone, issuing from the side of the cone of eruption, and later a little on the north-east side. On August 26th a radial fissure made itself visible, splitting the eruptive and great cones in a W. N. W. direction, and giving issue to a lava-stream nearly a third of the way down the slope of the great cone, not far from that of the 1895 opening. This stream had a total length of about 700 m. only, and stretched very little beyond the toe of the great cone. On August 27th a fresh opening occurred on the E. N. E. side of the cone, or rather at the foot, in the Val d' Inferno. The lava continued to flow for some months, shut in by the slopes of the great cone, the precipices of Monte Somma, and the Colle Margherita. It had commenced to build up another lava-mound, which Prof. Mercalli estimates to have a maximum altitude of 70 m., with its summit about midway between the base of the cone and the escarpment of Monte Somma,* and after flowing for over a year terminated on the 28th of September. This somewhat sudden arrest of the efflux of lava was followed by great activity

* " Notizie Vesuviana," 1904, p. 16.   Modena, 1906.

at the summit of the mountain, which, with variations, continued till the 27th of May, 1905, when two new mouths opened a short distance down the north-west side of the cone, close to the rifts of 1895 and 1903, and possibly may be but a reopening of one of the same old radial dykes. Strangely, though with a difference of altitude of 65 m., lava constantly dribbled from these two mouths for ten months, while the main volcanic chimney continued to show that range of variations that is so characteristic of Vesuvius in its more recent history. These variations at the rent have been described by Professors Mercalli and Lacroix as Strombolian and Vulcanian stages. My old definitions of cone-forming, or crater-forming, stages seem to me to be more precise. The analogy of Vesuvius with Vulcano is most unsatisfactory, the chemical nature, viscosity, and other physical characters of their magmas being so widely different as to make such a comparison most misleading.

I have given here a succinct account of the principal changes in the great Neapolitan volcano from its last paroxysm in 1872 down to the one I propose to describe. It would have been out of place here to enter into the more minute details, which can be gleaned from the writings of Scacchi, Palmieri, and Diego Franco, from 1872 to 1879, my own records published from 1879 to 1894, and since then those of Professors Matteucci and Mercalli.

Certain general principles, however, are, I think, to be drawn from this period in the history of Vesuvius, which the above-mentioned authors do not seem to have entirely appreciated. No less than five great solid masses of lava were added to the volcano; and, were it possible with any accuracy to estimate the aggregate volume of these, we might form some conception of the very considerable increase in the total bulk of the mountain. We might even hazard an estimate of the actual time taken to build up the whole of that striking feature of the Gulf of Naples—the type-volcano of the world.

These five great bosses grouped about the main cone, composed, as they are, of lava, with practically no fragmentary material, must constitute points of resistance to later outbursts near their sites. In fact, I have given a general description of these bosses and buttresses, as, where they existed in any great thickness, they certainly seem to have prevented the radial dykes of the 1896 eruption from reaching the surface; but I feel inclined to believe that for a considerable time in the future history of Vesuvius we shall see their tectonic influence. A fact they unquestionably show is that, at any rate so far as the 1883 and 1885 outpours are concerned, vast coherent lava-masses can consolidate on steep slopes and add to the building of a cone, provided the outflow is sufficiently *slow* and continuous.

ERUPTIVE PHENOMENA OF APRIL, 1906.*

April 2nd.—On this day the vapour-plume above Vesuvius was larger, and from time to time was darkened by the ejection of dust and sand. This, no doubt, was an indication of the formation of a new, or the extension of an old, lateral rift. In consequence of the withdrawal of magma necessary to fill this, the level of the lava fell in the chimney; and, as always occurs, the edges of the cone of eruption began to fall in, and to be re-ejected in a partially pulverized condition, mixed with fresh lava-cakes. The latter fact shows that the top of the lava column had not fallen very low. The fumaroles appeared more active; the seismic apparatus, such as it was, at the Vesuvian Observatory exhibited a state of agitation of the ground; and the telephone poles, Torre to Naples, from Ongino onwards "gave out a noise comparable to that of a cauldron of pitch boiling violently."†

April 3rd.—Seems to have passed without any very extraordinary or special manifestation, except that the explosions at the central crater were well marked. The *boati* were distinctly audible at the lower station of the funicular railway and even at a greater distance.

April 4th.‡—Early in the morning, at about 5.30 a.m. according to Mercalli, an opening occurred on the south slope of the cone near a spot marked Casotto delle Guide on the Carta Topografica Militare of 1903.§ This was on a radial fissure, as shown by clefts and fumaroles above the outlet. The outpour was of small importance, destroying the west bends of the Fiorenza path (see Pl. XXII.). The ejecta from the summit principally consisted of lava-cakes, showing that the lava was high in the chimney, and that there was little disintegration of the sides of the small inner crater. Professor Mercalli and others who were on the mountain observed a marked increase in the violence of the explosions near midday. All the morning the mountain was in a tremulous state, with of course more agitation at this time. Between 2 and 3 p.m. the lava-top must have sunk, probably filling the repeated extensions of the dyke or dykes. At the same time, the crumbling

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* There are many discrepancies even in the written records of scientific men, not to speak of casual observers. From careful inquiries and by the comparison of different chronicles of the events, I have endeavoured to construct what I hope to be a fairly accurate history of the successive incidents. My very detailed knowledge of the locality, and my intimate acquaintance with many of the observers, will, I hope, have assisted the correctness of this diary.

† Gargiulo, Gaspare, " Il Vesuvio e le sue eruzioni in Rapporto a Torre Annunziata " in " Il tributo di Riconocenza torrese a Maria T. T. della Neve."—Torre Annunziata, 1906, in 8°, p. 13.

‡ Prof. Lacroix has apparently confounded the 3rd and 4th of April. *Op. cit.*, p. 12.

§ That is, at an altitude of 1200 m.

in of the sides of the eruptive cone made great progress, as was indicated by the projection of the *accessory* lapilli, sand, and dust, which, with the increased discharge of vapour, rose as a fine pine-shaped cloud, bending to the south-west, and later, more westerly, so that in the late evening a greyish-black sand fell over Naples. Curiously, the lava that had been flowing from the north-west mouth for the last ten months was still doing so, so that after dark a red line was quite visible that night. This lava, which was rapidly covered by non-conducting fragmentary materials, was still hot, and exhibited blowing fumaroles in November, 1906, more than six months after the last outpour. It was represented by a strip of lighter-coloured dry dust, extending radially from the north-west base of the great cone towards the strait between the escarpment of Somma and the Colle Umberto. It is evident, therefore, that the lava-top was still above the level of these two openings or radial fissures, almost at right angles to each other. The new south stream tended to stop towards the evening.

April 5th.—At about midnight, the same new radial fissure, by extending, reached the surface of the cone, at a much lower level, about 800 m. only, at a spot marked on the above-mentioned map called Cisterna di Casa Fiorenza, or Pedicino. As is usually the case, this outflow was more abundant, coming from a lower issue. It crossed the Pedimentina and followed down the slopes, till it nearly reached the Casa Bianca. With a fall of nearly 500 m. in a distance of 2500 m. in thirty hours, it finally came to a standstill on the morning of April 6th. Simultaneously the old W.N.W. outflow stopped, and no doubt is now represented by a hollow dyke. During the night there was a state of relative quietness.

April 6th.—At about 8 to 8.30 a.m. a new rent appeared at an altitude of only 600 m. in the locality known as the Bosco Cognoli, that is nearly a kilometre to the east of the second opening. Professor Bassani and Dr. Galdieri* say they think this an extension of the same fissure. With this I cannot agree, unless the fissure meandered about in a circumferential rather than a radial manner. Carefully going over the locality, not only do I think this was a separate fissure, but I am rather inclined to fancy there was even another between the two and three mouths from which part of the extensive sheets of lava in this region flowed.† Professor Mercalli‡ speaks of new mouths in the plural, but does not indicate whether these were radially arranged or side by side. From these issued a flood

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* "Notizie sull' attuale Eruzione del Vesuvio."—Rend. R. Accad. Sc. Fis. e Mat. d. Napoli Fasc. 4° 1906, p. 3.

† Far more likely to my mind this row of mouths arranged circumferentially, and not radially, was due to a sill-like dyke, such as can be met with at Somma, and to that shown in fig. B, p. 185, sectionized in the new crater.

‡ "Grande Eruzione," etc.—Mem. d. Pontif. Accad. Rom. d. Nuovi Lincei, vol. xxiv., p. 7.

of lava very fluid, so that it spread out, but was of little thickness, in some places being nearly half a kilometre in breadth. By the early afternoon it had reached the Casa d' Aponte, that is about two kilometres. The irregularities of the ground of course influenced the direction and speed of the current. Near the mouths, on the steeper slope, with the rock less cooled, it is credited with having flowed 5 m. per minute; but as it advanced, cooled, and reached a feebler slope, its speed was less. Where the main path up to Casa Fiorenza crosses the five hundred and twenty-fifth contour-line, the flow divided. The western arm, broad at first, split into three tongues near the four hundredth contour-line, the two external ones stopping short, whilst the middle, as a narrow band, flowed due south, passing between the Masseria Izzo and that of Casa Torrentino, over the lava of 1754, destroying the Mass. C. Pallone, and stopping a short distance after having destroyed a good many gardens and vineyards. The eastern limb at first flowed in narrow strips on the steep slopes of I Cognoli, soon spreading into a broad sheet in the Rione Casarella and over the 1850 lava.

Near the Mass. Jaconelle and C. Napuano, which the lava destroyed, commences a narrow and small *vallone*, or ravine, which near the Mass. C. Rendina attains some depth. Into this, part of the stream flowed as in a narrow drain. The main stream continued on in the direction of the west end of Boscotrecase.

April 7th.—About 1 p.m. the explosions from the crater were violent and luminous, and fragments of scoria are said to have reached as far as the observatory. Early on this day, perhaps even before, lava flowed from a rift on the N. N. E. side of the cone. Wherever this lava did issue, it must have been from a point very high on the cone, for I found it sheared by the lip of the new crater, immediately after the eruption. The very luminous explosions just mentioned would certainly point to the lava-level still being very high in the chimney. In the early part of the day, there was relative quiet, possibly in consequence of relief given by the N. N. E. outflow. The southern stream moved on slowly, so that at about 3 p.m. it was stopped on a level with the Cemetery of Boscotrecase, that is, about half a kilometre from the town. Crowds of people went to visit the lava, thinking that the eruption was at an end, and those people of Boscotrecase who had removed their furniture were taking it back. During the morning of the 7th, Dr. Brunhuber observed an active mouth to the east of I Cognoli, which gave out two streams of lava flowing eastwards, towards Terzigno, the northernmost flowing as far as the Bo. Vracciaro and Bo. Fontanelle, the other through the Rione Torrioni towards Bo. Molara. Soon after 4 p.m., the explosions from the central crater became more violent, being audible from Naples. Prof. Mercalli says: " The material ejected was nearly all incandescent and fluid, and in broad jets, and attaining from one to two kilometres above

the level of the crater-edge, and succeeding each other so rapidly (two or three minutes' intervals) that they formed a continuous fountain of fire. The very large diameter of the fire column was due to there being two mouths of explosion, as sometimes one could see contemporaneously two fiery jets."* The whole of the great cone was covered with a mantle of fire. At 7 p.m. the violence of the ejection was much increased, and the rumblings and reports of the volcano were much louder, accompanied by variously shaped electric discharges and thunder. At 10 p.m. some lapilli began to fall at Ottajano. At 10.30 to 10.45 p.m., with terrible reports, mouths at I Cognoli and that of the Terzigno burst forth in activity, with the projection of incandescent scoria. One of the Cognoli mouths gave forth a flood of lava that swept down the steep slopes like water. Prof. Mercalli says it flowed a kilometre in the first 15 minutes. The *bocca* opposite Terzigno gave out such a flood of fluid that the stream that flowed towards Terzigno covered 4 kilometres in half an hour on a relatively gentle slope. The *bocca* at Contrade Ciaramello again became active, and gave forth a copious stream of lava, which added to the flood. It followed the same route as that of the day before and the morning of the 7th, except that it added to the breadth and extent of the sheet. Opposite the Casa d' Aponte it left a small island uncovered and threw off two or three tongues, the middle one of these, a voluminous one, to the east, towards the Rne. Pozzole and Mauor. Travelling due south, in a broad torrent, it further buried the Mass. Jaconelle and C. Napuano. Here part of it followed the ravine already mentioned, down which it poured, filling the gorge completely, and in some cases overflowing the banks. Later in the day, as the flood diminished by the outflow at the lower end, it left this ravine with morainic fringes of scoria on the edges of the valley, the banks smeared with a sheet of lava and a crust occupying its bottom (see figs. A, p. 160, and 8, 9, Pl. IX.). On reaching the lower end of this drain, and a flatter, broader, less-confined space, it spread out and destroyed a large number of houses in Boscotrecase. It cut the main road in that part of the town known as the Oratorio, flowing into the cutting of the Circum-Vesuvian railway, crossing the two new roads known as the Strada Nuova, and stopped before daylight of the 8th.

The main stream, as a broad sheet, swept on, destroyed the western end of Boscotrecase, following down the Vallone del Oratorio; it reached the north-east end of the Cemetery of Torre Annunziata, spread around and enveloped the Mass. Sannino. It had crossed and further destroyed a part of the Circum-Vesuvian railway. Some time during the evening, the mouth near the Casa Fiorenza again became active and emitted a good quantity of lava, which flowed over that of April 5 and 6, that issued from the same spot, and as a long

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* " Grande Eruzione," etc.—Mem. d. Pontif. Accad. Rom. d. Nuovi Lincei, vol. xxiv., p. 9.

narrow tongue poured down the slope past the Casa Bianca, and stopped at about the 375 contour-line.* The flow itself did not reach this point till about 3 a.m. the following morning; but as I shall show later on, this must have been the stock of fluid rock already without the mountain, or in the lateral rift. About an hour before midnight, a slight calm appeared to have occurred, due, no doubt, to a rapid fall in the lava-level, in consequence of an abundant outpour at the different lateral rents.

April 8th.—Twenty minutes after midnight, with a loud report, a great rift, 3 kilometres in length, split the mountain parallel to the lava of Terzigno. Near the middle of this rift, a crater was formed, ejecting scoria, etc., with such force as to equal in volume that of the central crater. Half an hour after midnight, explosion after explosion occurred from the great crater with terrific violence, shaking the whole region, so that houses were in a constant state of tremor, and people were awakened. The column of ejecta was enormous, and the electric discharges were continuous, so that, in addition to the explosions of the mountain, was added the constant noise accompanying these lightnings.

There seem to have been two violent convulsions, one at 31 minutes after midnight, and one at about 2.40 a.m. Many witnesses assert that during these early hours the ejecta were somewhat luminous, and appeared more especially so towards Ottajano. The *essential ejecta* of the nature of that described later on no doubt did issue with sufficient heat to be luminous; nevertheless the brushwood buried in it, at the Punta del Nasone, was not burned, so that as the volcanic material spread through the air and vesicularized, its heat was no doubt rapidly used up in this process. As the night advanced, all was one vast dark mass of stone-laden atmosphere. It was during these early hours that the ejecta were chiefly *essential*, which, carried in a north-easterly direction, spread over Somma, Ottajano, S. Giuseppe, and away over the Campanian plain to Nola, Palma, Sarno, damaging also Terzigno, Piazzollo, Cinquevie, and S. Gennaro di Palma. Crossing the Apennines and the Adriatic, the finer dust reached as far as Montenegro. Towards dawn, the ejecta were chiefly *supplementary*, or *accessory*, being derived from funnel-like paring of the walls of the upper part of the chimney by the evolution and escape of vapour from gradually increasing depths, and formed the dark mass in the atmosphere, as mentioned above. The edges of this growing crater were of course constantly falling in, only to meet the uprushing column of vapour by which the materials that had composed them were carried to very great heights. It is estimated that during the day the column of fragmentary materials attained over 7,000 metres. Prof. Matteucci and A.

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* All localities, heights, and contour-lines refer to my geological map. Geological Map of Monte Somma and Vesuvius, with a short and concise account, &c. 1 : 10,000. London: Geo. Philip & Son, 1891, in 6 sheets.

Fiechter * give the maximum height attained by the smoke pine in April as 10,000 to 13,000 metres. No day is given, but I presume it was on the 8th. This column bent over in a north-east direction, continuing the destruction of Ottajano, S. Giuseppe, and the other towns in that direction.

Great discrepancies exist between the different observers as to the cause of this bending over of the column of ejecta towards the north-east. De Lorenzo attributes it to the south-west wind ; but, as will be seen by the appended table, the wind at the Observatory of Capodimonte was absolutely in the opposite direction, and blowing at from 17 to 20 kilometres per hour. But of this we shall speak in the general discussion of the phenomena. During the day of the 8th a vast crater was excavated in the great cone of Vesuvius, half a kilometre in diameter, and probably extending far below the level of the Pedimentina. The enormous mass of materials derived from this was spread over the slopes of the mountain, constituting at the base of the cone a gigantic accumulation of the larger masses that fell within short range of the volcanic axis, or that collected on the cone itself, and from time to time slipped to its base. During all the day of the 8th the whole mountain was enveloped in an impenetrable cloud of cocoa-coloured dust. Above this, at frequent intervals corresponding with land-slips of the crater-edges, followed by the expulsion of the loose materials, great pine or cauliflower-like masses rose above the general dust-cloud, of a darker and more leaden colour. This spread out, and was principally carried towards the north-east quadrant. In fact, in the morning most of the accessory lapilli and blocks were ejected, which, from the larger quantity and greater density, did the greatest damage to Ottajano and the neighbouring towns and villages. The fall of dust that had off and on continued in the province and town of Naples since the 4th became still more abundant and of the cocoa-colour of which we shall speak. The shocks and vibrations continued all day. Added to this was the thunder from the lightnings that played continuously in the dust-cloud. The violence of these noises was such that they were heard far and wide, reaching into the Puglias, and even ships in the Adriatic were enveloped in thin clouds of dust. Towards evening there was some diminution in the violence of the outbursts. It was, however, not till 10 p.m. or later that the lapilli-shower stopped at Ottajano.

April 9th.—All through the night there was marked eruptive activity, but with progressive weakening in its violence. Nevertheless, the explosions were still audible in Naples till about 9 a.m. The bending over of the column of ejecta to the north-east had stopped during the night. The forces of explosion also were becoming exhausted, so that the materials that could be ejected became finer and finer. The north-east wind seemed to make headway, and carried these finer

* " Appunti sulla Eruzione Vesuviana, 1905–1906."—Bull. Soc. Geol. Ital., vol. xxv., 1906, p. 847.

materials away in the opposite direction.   During the day heavy clouds of sand and dust fell over that sector of the mountain between Portici and Torre del Greco.   So dense was this cloud that the darkness was compared to that of a tunnel.   The base of this sector would measure from 3 to 4 kilometres at the line of the coast.   Fine dust was still falling over Ottajano and that district during the whole day.

April 10*th.*—The ejection of fine lapilli around the cone, with sand and dust at greater distances, continued, but the fairly strong N. E. and N. N. E. winds carried most of it over the towns and sea to the south-west of the volcano.

A good deal of the components of the dust-clouds was still being ejected, but much of the dust in the atmosphere was produced by the slipping down of loose materials on the surface of the cone.

On the 10th it was possible for the first time to see the great masses that had not only slipped off the cone that had been deposited on its slopes by the eruption, but also the great scars over the lateral outburst of the 4th, 5th, and 6th April, on the south flank of the cone, between the lava buttresses of 1883 and 1885.

These slips continued without intermission for days; and when I visited the volcano on April 26th, they were still in progress, but by that date the most unstable collections had been dislodged.

By the afternoon of this day, the 10th, the great lava-stream of Boscotrecase-Torre Annunziata had completely stopped, though that towards Terzigno was still showing a little movement.

Strangely enough, about midnight, one of the Bosco Cognoli mouths emitted some fresh lava, that flowed over the earlier streams for some distance towards Bosco.

April 11*th and* 12*th.*—The dust of the 8th, 9th, and 10th always maintained a reddish colour, most comparable to that of cocoa.   On the 11th there were fairly strong explosions at rather long intervals.   Early in the forenoon there was a good deal of terrestrial movement recorded by the seismic apparatus at the Observatory.   Towards evening Naples was at last delivered from falling dust, as were likewise Portici, Torre del Greco, and Torre Annunziata.

April 14*th.*—A shower of grey dust, some centimetres in depth, fell at San Giuseppe and Ottajano.   Falls of dust were also recorded at Collina, Strocchia, Boscoreale, and Somma.   A slight earthquake was felt at Ottajano and Terzigno.

April 15*th.*—At 2 p.m. a heavy shower of dust began falling at Ottajano, Boscoreale, Boscotrecase, and Torre del Greco, causing intense darkness.   Some dust fell at Portici, Resina, San Sebastiano, and San Giorgio.

April 16*th*.—Relatively quiet; seismographs quiet.

April 17*th*.—With slight seismic tremors, quiet continues; some dust being ejected, falling to the north-east and east.

April 18*th to* 30*th*.—Gradually the output of the grey dust diminished. The crumbling in of the crater-edges and sides still went on apace, and more and more blocked up the volcanic chimney, so that the puffs of vapour and dust became feebler, and the intervals increased between each one. This condition prevailed when I reached the crater-edge at the end of the month.

For many days after the eruption any attempt at approaching the base of the cone was attended with great danger, as one sank in the hot dust and lapilli. A few unwary and unpractised persons who made the attempt were severely burned. It was not till a good rainpour had cooled and set the surface that walking was practicable during this memorable month of April. There are considerable discrepancies as to the sequence and interpretation of events between the different observers; but the difficulties of observation are clearly so great that all excuses may be made for those who have attempted to record this great convulsion of Nature. One observer cannot be awake both night and day; he cannot be at many spots at once; dust and vapour often cut out his view; and, above all, those who know the people of this region are fully aware of the slovenly state of their observational powers and memory of events, and their uncontrollable tendency to exaggerate.

General Considerations.

Vesuvius had for a considerable time been in what I would call the *ordinary or chronic Vesuvian state.* I would define the Vesuvian state of a volcano as that slightly varying activity at the top of the main chimney, the ejection of incandescent, pasty lava-cakes, building up a cone of eruption with a small, steady, almost continuous lateral outflow of fluid magma as small lava-streams. When, after a period of no lava issue, a lateral outburst occurs, a rapid outpour takes place, with the sudden fall of the lava-level in the volcano chimney, the activity passes from the *essential* lava-cake and *cone-forming stage* to that of the projection of fragmentary, *accessory ejecta,* and the *crater-forming stage.* As already stated, Professor Mercalli has referred to certain conditions of Vesuvius as Strombolian and Vulcanian. It is more especially concerning this last adjective that I would strongly protest. I know both volcanoes well, and I saw a good deal of the eruption of Vulcano in 1889. I have no hesitation in saying that there could hardly be a worse comparison of the phenomena of Vesuvius than with that of an acid volcano usually in a chronic-solfataric state, bursting forth with explosions from a highly viscous magma, and extending its eruptive period over months, and without any outflow

of lava. Vesuvius, in the whole of its history, either recorded by man or decipherable from its rocks, gives no evidence of any other grades of activity than those which I have pointed out during the last quarter of a century, and which are marked* on the following scale :—

Scheme of Grades and Varieties of Activity in Volcanoes.

* 1.—*Mephitic* (acid and basic).

* 2.—*Fumarolic* (acid and basic).

* 3.—*Solfaratic* (acid ; rarely basic).

* 4.—*Strombolian* (basic) . . . { 4a.—Ordinary chronic activity ; lavas rare.
{ 4b.—Paroxysmal outbursts very rare.

* 5.—*Vesuvian* (basic) . . . . { 5a.—Ordinary ; lavas abundant.
{ 5b.—Paroxysmal ; frequent.

* 6.—*Icelandic* (basic ; rarely acid) { 6a.—Quiescent.
{ 6b.—Paroxysmal, with great outflows of lava usually.

7.—*Vulcanian or Pelean* (acid) . { 7a.—Solfaratic or fumarolic.
{ 7b.—Paroxysmal.

8.—*Plinian or Explosive* (acid or basic). (Pumice.)

9.—*Phlegræn* (acid ; more rarely basic). Production of a volcano, usually explosively by a single eruption, or rarely more than one at a long interval.

The present eruption, therefore, cannot be better described than of the *paroxysmal Vesuvian degree* following upon *an ordinary Vesuvian degree.*

The more I study active volcanoes the more I become convinced that the actual output of material for any given one is sensibly uniform and continuous over long periods, but of course most variable for short ones. That uniformity is not so marked if our observations are limited to a short period. Years ago I demonstrated that by the study of Vesuvius and its products we there had admirably illustrated the fundamental principles of *volcanic action.* I have demonstrated that in what we include under that term there are two groups of phenomena quite different in themselves, but so linked together that vulcanologists, with few exceptions, have failed to unravel them.

It is by the incontrovertible records left in the structure and composition of the volcanic products, that it is relatively easy to interpret these various phenomena. Although it is a quarter of a century ago since those principles were laid down, volumes of unsupported hypotheses have been launched on the public.* This great misfortune is doubtless attributable to the persistence of petrographers

* "The Geology of Monte Somma and Vesuvius," Quart. Journ. Geol. Soc., vol. xl., 1884 ; and "The Relationship of the Structure of Rocks to the Conditions of their Formation."—Sci. Proc. Royal Dublin Society, vol. v. (N. S.), 1886. "The Causes of Variation in the Composition of Igneous Rocks."— Natural Science, vol. iv., 1894, p. 134. "Extension of the Mellard Reade and C. Davison Theory of Secular Straining of the Earth to the Explanation of Deep Phenomena of Volcanic Action."—Geol. Mag., Dec. iii., vol. vii., 1890.

in devoting their whole attention to massive rocks instead of to the fragmentary ejecta of volcanoes.

I shall attempt to recapitulate my theories in as concise a form as possible, and see whether they are borne out by the Vesuvian manifestation under consideration. If we examine the *essential ejecta* of either a paroxysmal or explosive eruption, we find that the first material ejected, be it scoria or pumice, was accompanied by the greater evolution of gases, was more vesicular, more vitreous, and less microlitic, and devoid of post-eruptive crystallization. The explanation of this rock-structure which I gave was that the fused rocks of the magma in the upper portion of the canal, where the walls were aquiferous, were able to take up and *dissolve*, in relation to time and pressure, the largest quantity of water and any salts accompanying it. At the moment of the outburst and the relief of pressure, the enormous loss of heat-energy in the passage of super-heated water *in solution*, and therefore of small bulk, to the state of voluminous expansion of steam, meant the rapid solidification and cooling of that portion of the magma which had held it. The fragments of frothy, otherwise pumiceous or scoriaceous magma, therefore, will be so rapidly cooled that the residual glass, in which are enveloped the intra-telluric crystals, will have little or no time to devitrify into extra-telluric crystals or microliths, as in the scoria *a* (figs. 26, 27, Pl. XVIII.). As more magma rises in the volcanic chimney, it will have come from greater depths, where the enclosing walls will be of less aquiferous rocks, and where also its initial temperature will be higher from less extensive loss either to the walls, or in the act of dissolving out water from them. The amount of loss of heat-energy from expansion of the smaller quantity of water dissolved in it will likewise mean slower cooling, slower vesiculation, slower ejection, and greater time for residual glass to devitrify or individualize into extra-telluric crystals and microliths, so that a darker, harder, heavier scoria or pumice will overlie the lighter-tinted, less heavy, or more vesicular ejecta that had fallen around the volcanic rent as *b* scoria (figs. 28, 29, Pl. XVIII.).

Later, as a magma still more removed from saturation by water rises from greater depths, the loss of heat-energy will be still less, more time will be given for extra-telluric crystal and microlitic individualization (essential scoria of *c*, fig. 30). This crystallizing and microlitizing process may go on to such an extent that the entire conversion of the residual glass may be so complete as to abolish its function as a cohesive cement, and the whole magma-mass may issue as an incoherent crystalline dust. Such dusts are the final phase in many explosive and in some paroxysmal eruptions. It is out of place here to touch upon the *accessory* or *accidental ejecta* that may in greater or less quantity be carried out of the crater during such violent eruption.*

* Consult my paper, " On the Fragmentary Ejectamenta of Volcanoes."—Proc. Geol. Assoc., vol. ix., pp. 421–432, 1886.

Finally, from still greater depths the magma may rise and flow out as a continuous mass, because it will have begun to move from the deeper part of the volcanic chimney, with a still higher initial temperature, and with little or no loss of heat from the acquisition of water or excessive vesiculation or expansion of the latter.

These facts, which I first discovered at Vesuvius,* but which can be seen in any volcanic region, and especially amongst basic rocks, where they are more clearly discernible, point, in my opinion, to the fact that the 'explosive, expansible manifestations of volcanic action are a purely *surface phenomenon*, and dependent on the porosity of the outer layers of the Earth's crust, and thus they are more or less aquiferous.

Unlike this surface volcanic action, which can be read from the rocks, the deeper volcanic phenomena are much more hypothetical. Whether we believe the Earth to possess a cooling crust, containing a fluid rock, or a cooling crust around a highly incandescent but solid nucleus, potentially fluid if under reduced pressure, we have conditions which will give rise to fracturing. Such tearing will take place in the inner cooling shells of contraction, and will extend upwards to the zone of no strain, and beyond it between the blocks or islands of compression. Any such fracture will, of course, be simultaneously filled by the fluid igneous paste beneath, or, if such does not exist, by a highly incandescent rock that would become fluid by the relief of strain set up in the neighbourhood of the fissure. Where the upper limits of such rifts reach aquiferous strata, filled by the liquid or liquified rock from below, the second series of conditions favourable to surface volcanic phenomena will take place. When a continuous communication exists in an active volcano, a state of relative equilibrium will ensue, by which, in consequence of the fairly regular secular cooling of the Earth's crust, a uniform amount of the fluid nucleus will escape. In a general way we may say that the shrinking part of the crust will squeeze out through rifts in itself a fairly regular and uniform amount of fluid igneous paste. Such regularity and uniformity will be disturbed by the different variations in the state of the upper portion of this volcanic canal; and it is to those conditions that we will now direct our attention, as illustrated in this Vesuvian eruption.

For a good many years the upper portion of the main canal of Vesuvius—that portion we may conventionally call the chimney of the volcano—has been occupied by a mass of igneous magma in a fluid state of ebullition. Let us for a moment consider what influences are at work upon such a mass, and what modifications it would undergo.

There will be from the prime source below a fairly uniform accession of material, so that there will be a constant tendency for the lava to overflow from the summit of the cone. As a matter of fact, this did occur frequently. But the actual upward

* *Op. cit.*, Quart. Journ. Geol. Soc., vol. xl.

termination of the volcanic duct, the cone in fact, is so incoherent that rarely is it able to withstand the out-thrust of the fluid column that it encloses, and a lateral outlet is formed. The overflow will be proportional, therefore, to difference of level between the top of the lava-column and the lateral outlet; and, in fact, where other disturbing factors do not interfere, general experience shows this to be the case. When such a lateral outlet exists, the *primary* overflow (by which I mean that due to the steady accession from the prime source) will drain off that excess. When the lateral opening is first established, in addition to this excess there will also be the fluid rock occupying the chimney above the level of the side tap, so that when this is established there is a big outpour, followed by a constant dribbling. To be more concise, the output from a lateral rent depends on:—

(*a*) Amount of lava above the lateral outlet.

(*b*) The secular output of lava.

(*c*) The rise of magma due to its expansion from increased vesiculation after the relief of pressure from the fluid column above it has drained away.

This was, in fact, the actual condition that so frequently prevailed during the period from 1872 to 1906, and, of course, has been the dominant characteristic of Vesuvius for some centuries. It is to this mechanism that the lava-cones, bosses, and buttresses of 1883, 1885, 1891, 1895, and 1903 owe their existence. This outflow is not, however, without some sources of perturbation—such as the increasing viscosity of the lava, the gradual blocking of the outlet by the addition to its walls of congealed rock, such as we see in hollow and other dykes, the formation of another outlet at a lower level on the same radial rift, or the formation of a new one. The effect of such disturbing influences is illustrated in the case of the outpour of lava on and after the 27th March, 1905, where two lateral openings gave forth fluid rock, notwithstanding a difference in altitude of 65 m. During the great eruption itself the same thing occurred; lava issued at very considerably different levels.

In the ordinary Vesuvian activity of a volcano, I repeat that two variations are constantly observable—those which for many years in my writings I have described as the lava-cake and cone-forming stage, and the dust and lapilli and crater-forming stages. The first is characterized by the emission of fragments of incandescent plastic scoria, or purely *essential ejecta*, the second by the expulsion of hard, cooled, broken-up fragments of the crater-walls, or purely *accessory ejecta*. The second is usually present when the ordinary Vesuvian grade of activity tends to pass to a paroxysmal stage.

The first or cone-forming stage is due to the lava-level line being very high in the chimney, through and from which the vapour bubbles out. In the act of

these large bubbles bursting at the surface of the fluid rock, coarse lava spray is detached and ejected, and constitutes the lava-cakes that are constantly scattered around the vent by the explosion (bursting of gigantic gas-bubbles). The collection of these lava-cakes composes the principal materials around the vent, and builds up the cone of eruption. While the outer slope of this cone of eruption is usually that of the angle of repose of such materials, the inner face is vertical and the lava-column is sufficiently high to support it, or solder its constituents together. When a radial rift splits the cone, as so frequently occurs, there will be a sudden fall of the lava in consequence of its filling such a cleft. Still more, if that cleft reaches the surface of the cone at some spot, and fluid rock issues, there will be a still greater fall of this central lava-column. The support of that column will be removed from the inner surface of the chimney; and the cone of eruption and the edges will begin to crumble in. This destructive action will be further accelerated by the escape of vapour from the lowered surface of the lava. In fact, I shall show presently that the amount of vapour in such a case is even increased. The escape of these gases under some constraint in the now empty portion will add to the degradation of the walls, which continue to crumble in, gradually excavating a conical hollow which we call the crater.

If the lava-surface has fallen very low, the explosions of gas may be insufficient to eject lava-cakes beyond the new crater edge; but the crumbling materials will be ground and more or less pulverized and ejected, so constituting the dust-forming stage with the expulsion of these *accessory ejecta*. There are all gradations between the cone and crater-forming stages, as there are between the ejection of *essential* materials, as lava and scoria cakes, or of old broken-up fragments and dust which constitute the *accessory ejecta*.

By the constant ebullition of lava in the chimney we have two sources of the vapour. Part will be derived from the upper lava itself, which it had acquired at greater depths and brought up with it, while other vapour is no doubt the excess of that which the magma deeper down in the canal continuously evolves, and which would rise through the upper mass. Provided the output is slow, then there will be a tendency, by the increase in viscosity of the upper portion of the lava column, to augment the resistance to the escape of vapour from greater depths. Then the tension of the magma will increase in the deeper parts. A struggle will then take place between the increasing viscosity of the upper portion of the column which might go on to complete solidification, and the rising tension of the magma deeper down. If such a state of things has been going on for some time—we will suppose not to the extent of solidification of the upper part of the column—and if by the formation or reopening a lateral outlet takes place, and most of the obstructing plug is drained out, removing the pressure from that of the high tension magma below, it is obvious that violent vesiculation and

ebullition will take place in the now relieved deep-seated magma. These, in fact, are the conditions that prevail in what we classify as paroxysmal eruptions, and this is what actually happened at Vesuvius during the late eruption.

As we proceed to examine the phenomena and the products of this last eruption, we shall see that the evidence they afford is that above described.

It is probable that the cooling, crystallization, and steady increase of the viscosity in the lava of the chimney had gone on at such a rate that the overflow by the lateral outlet was insufficient to carry off this obstructing, pasty lava, and therefore its presence interfered with the perfect freedom of vapour escape from lower down. The result of this would be a disruptive tendency, which resulted in the formation or reopening of a number of radial fissures, splitting the cone in different azimuths, and as viscous lava filled these, fresh, more gas-bearing magma rose, ebullition went on more actively, representing the increased activity of the earlier days of the eruption. These lateral openings at a relatively low level were so efficient in giving exit to the upper portion of the obstructing lava that this was rather suddenly removed, so that at the climax of the eruption deep-seated, more aquiferous magma, now relieved of its overlying burden, rose in the chimney, and was, in consequence of the rapid and violent ebullition of effervescence, projected to great heights, as the blackish-brown or lighter vesicular scoria, or *essential ejecta* that was scattered over the flanks of the mountain in the earlier hours of April the 8th. This was followed by magma coming from still greater depths, having acquired less water, and consequently being richer in heat-energy at its eruption. This magma is denser and more micro-crystalline in consequence of slower cooling. This constitutes the second stratum of black scoria scattered around the mountain, and especially over Ottajano and neighbourhood in the early morning. Just as in a bottle of champagne newly opened, when the first frothing-up has subsided, so in the morning of the 8th the ebullition of the magma could no longer reach the crater-edge, the "fountain of fire" was replaced by the "fountain of stones." The crater-edges having no support were now more extensively torn and pared away by the vast amounts of gases still escaping, which projected the resulting materials high into the atmosphere from which they fell, and constituted the third and major part of the breccia and lapilli stratum, such as we see especially in the north-east section of the volcano. This represents the eruptive period from the morning to the evening of April 8th. Not only did the escaping gases pare, excavate, and tear away the walls of the chimney, converting it into the fine crater we now see, but slips of the tuff and ash along its edges precipitated the materials down the chimney, in face of the uprushing vapour which projected them many kilometres into the atmosphere.

Most of these materials have been subjected, between the time of their

formation as part of the great cone and their breaking up and ejection, to intense and continuous fumarolic action.   The result is that the dominant and prevailing tint is brick-red, which tint characterizes the bulk of the enormous breccia deposits at the toe of the great cone, as well as more than two-thirds of the stratum that buried Ottajano, San Giuseppe, and the neighbourhood.

The escaping vapour that at first carries the *accessory* breccia and lapilli high into the atmosphere, will gradually become less and less, till any coarse material can reach little beyond the crater-rim, and most of the remaining explosive energy is employed in the grinding-up, by the issuing gases, of the fragmentary debris tending to fall down the chimney.   The escape of these would still be sufficiently strong to carry upwards, in the highly heated column, large quantities of the fine resulting dust, to be wafted to one side or the other by the prevailing air-currents.

This product is represented by the cocoa-coloured dust that was ejected from 10 p.m. on April 8th till April 13th.   The dust then quite suddenly changed colour to a light-grey, that gave to the mountain the peculiar snow-covered effect. Here I have only one explanation to offer, and that one I can only qualify as purely hypothetical.   Till the 13th it is probable that the chimney was still patent between the surface and the top of the magma, that the explosions were still able to deal with the main part of the falling materials, so that the passage remained open.   About the 13th, probably, the continuous slipping of the crater-edges finally blocked the channel for the free evolution of gas, which was only able to escape from time to time, carrying with it the finer portions of the debris slipped in from the crater-edges, and which, at the line of truncation of the cone, have been little reddened by fumarolic action.   It is also possible that the colour may have been changed by the filtering through the plug of loose materials by the volcanic vapours, producing a slight fumarolic action on each grain, so converting the peroxide of iron into chlorides, sulphates, or even sulphides.   The analyses of the soluble parts of these dusts afford us uncertain information; but only small traces of acid vapours would be sufficient to change the colour, and this seems to be the case, as indicated in the analysis by Casoria (p. 174).

Before leaving this general survey, there is one other slight difficulty that requires consideration.   After the principal outpours of lavas had practically stopped, and after the great paroxysm by which we should have thought the lava-level had fallen below the level of the lateral outlets, we find recorded that about midnight of the 10th, the "bocca" above Terzigno again emitted some lava, that flowed over that already solidified.   The explanation of this phenomenon that offers itself to one's mind is that that lava was the remnant left in a radial dyke, or sensibly horizontal sill, which acted as a reservoir, the contents of which was squeezed out by settlement of the mountain.

Such, then, is a general review of the sequence of events that this paper is intended to record. We shall now proceed to examine the different products of the eruption, and see whether we can obtain from their physical character a confirmatory record of what took place.

THE LAVAS.

I have examined the different lava-streams to see if it were possible to find any marked difference between those emitted early or late in the eruption, or whether those that issued at a higher level or a lower one exhibited variations in character that might afford us any valuable information. Specimens were collected of the extreme scoriaceous crust, both at the top and bottom of the stream and one or more from the interior—that is so far as circumstances would allow. There is in all lava-flows a considerable difference between the crust that cooled quickly and the heart of the stream that may have taken months to completely solidify. That difference is that the surface shows an abundance of residual glass, whereas practically all of it has become converted into a microlitic base in the interior of the stream.

Such variations are to be met with in all the streams of Vesuvius, and the observer has to be careful that any particular flow is not considered different from another by the examination of too limited a number of specimens. In some of the upper flows it is quite impossible to examine the real interior; but large slabs can occasionally be met with and broken up—the most central part being used for study.

The general character of these lava-streams is, that they possess an extremely rough scoriaceous surface (Pl. XIII.), quite of that kind which Dana called the *aa* type—a name that I have since applied to other lavas than those of the Sandwich Islands, and which is being now adopted by other geologists. These new lavas are very similar to many others emitted from Vesuvius in late years. Where flowing over a fairly level surface, they have the usual steep sides, and in a few spots have left the usual scoria-morainic borders. The depths vary from less than a metre to three or more, according to the angle of slope and the fluidity of the lava. In depressions, near obstructions, or where several streams are piled one above another, naturally the depths are much greater. Some interesting phenomena were displayed in the flow of the lava.

Near its source the lava seems to have shown great fluidity. One observer credits it with a speed of 67 metres per minute, and another 134 metres per minute. Admitting that this last estimate is exaggerated, it must be conceded that the fluidity was very great. When it had cooled somewhat, and burdened itself with scoria, its progress was of course much slower. As the eastern main branch that destroyed Boscotrecase flowed through the narrow ravine, it retained

great fluidity in consequence of the small cooling surface, for it must have been for a considerable distance from 5 to 12 or more metres in depth. The flow through this narrow valley was very instructive (see figs. A, 8, 9, Pl. IX.). The ravine at one moment was filled above the level of its banks; but the cohesive, viscous nature of the lava, and the quantity of scoria it cast off at its sides, kept it together. The scoria moraines are very striking in some parts (figs. 8, 9, Pl. IX., fig. 13, Pl. XI., and AA fig. A), especially at curves. The fluid rock left smears (BB) of itself, in consequence of the cooling and shearing as it flowed onwards. When the flood had passed, the main mass drained out of the ravine, leaving only, as it were, a small ingot (C) at the bottom. This was an exception to the lava in general of this eruption : in some parts it showed the corded-folded "*pahoehoe*" surface, instead of a rough, scoriaceous *aa* structure. This was, no doubt, due to the lower portion having time to liberate the major part of its vapour more gradually from the slower cooling, and the carrying on of the surface scoria by the falling, advancing flood.

Figure A.—Diagrammatic Section of Valley through which the Lava flowed above Boscotrecase.

LL.—Level of lava at full flood.
AA.—Scoria moraines formed at sides at full flood.
BB.—Smears of cooled lava on ravine walls during full flood.

CC.—Residual ingot of lava remaining after flood had drained away.
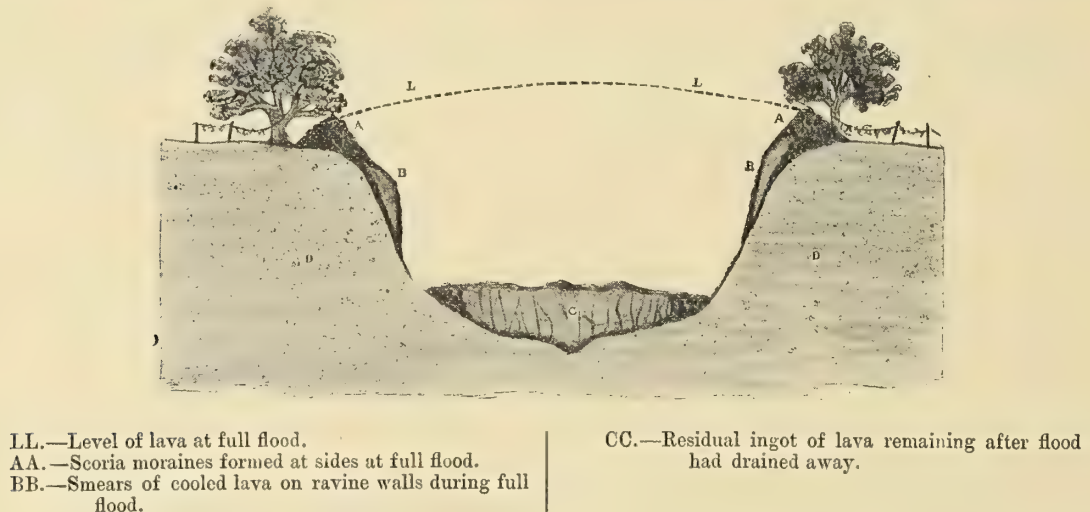
The great fluidity of the lava when newly poured out, and in considerable bulk, permitted it to flow with great facility in very narrow channels (figs. 8, 9, Pl. IX., fig. 12, Pl. X., fig. 14, Pl. XI., fig. 16, Pl. XII.). At one spot it filled and followed the Circum-Vesuvian Railway-cutting (fig. 15, Pl. XI.), passing under a stone bridge with ease. As the flow slackened, the rapid loss of heat made it so viscous that the obstruction of the arch, compared with the cutting in which it was flowing, eventually arrested its advance. It then collected behind the bridge, and had already built up such a pile that the whole bridge had started to be pushed bodily on. At this point, however, the lava supply failed, and left things as seen in fig. 19.

The effect of obstructions is well illustrated in figs. 15, Pl. XI., and 16, Pl. XII.; in one case (fig. 16), although the lava in the street without reached above the level of the first floor, and flowed on a great distance, yet, after the destruction of the wooden gates, it only advanced a comparatively short distance into the courtyard of the Villa Michele and Teresa Borosio. Where the lava followed streets, a similar effect was produced, unless the quantity was very great. The actual depths of the flow, on fairly level ground, can be roughly judged by the two figs. 12, Pl. X., and 13, Pl. XI. Another plate shows a row of houses, near Oratorio (fig. 17, Pl. XII.), which were of one story high, the "lastrico" roofs only showing, which would give an average depth of about 4 metres. When houses and walls were in the course of the stream, they could not long resist the pressure, and were soon pushed over, and the fragments carried on by the current. The effect of the lava where crossing a wall-lined road is shown in fig. 11, Pl. X. Here the wall was in the act of being bodily pushed over, when the supply of lava stopped. In certain spots the lava was so fluid that it flowed through the lower story of a house without overturning the building; but where this could take place, it was favoured by suitable doors and windows in the line of flow, and strongly built walls that were able to withstand the onslaught.

Where trees of some bulk were enveloped, these were usually burnt through to the depth of the enclosing lava. Sometimes they were still to be seen standing, held up by the brand of carbonized wood, held in place in the thick scoria-stratum above the lava. In other cases they fell over, but were not burnt on account of the bad conductivity of the scoria-covering. Most, however, were completely incinerated, leaving no trace behind.

The dry wood of houses was, of course, rapidly burnt up. Masonry was little altered, unless comparatively small pieces were enveloped in the lava, and remained there during the weeks of cooling. So far, little of such pieces have been recovered, as extensive quarrying operations are only now begun (Nov., 1906). I found some interesting changes, however, in the ordinary red tiles, which have become a light pea-green, and mortar also has assumed a greenish tint. The investigation of these changes might afford some interesting facts.

The surfaces of the lava-streams are abundantly strewn with the irregular globular masses that I described as flotation-bombs. I showed many years since[*] that these are not true bombs, but only masses accidentally caught up in a lava-stream, and enveloped in a crust of the fluid rock that they congeal around them, and are carried up to the surface, partly by their lightness, as they usually contain hollow spaces of one sort or another, and are also floated up by forming a surface for the liberation of vapour, just as lemon-pips float in an effervescing lemonade. I think a still better term for them than flotation-bombs, as they are

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[*] "On the Fragmentary Ejectamenta of Volcanoes,"—Proc. Geol. Assoc., vol. ix., pp. 421–432,

not bombs, would be *volcanic dumplings*, as their mode of formation is identical with the method of preparing that dish.

The contents of these *dumplings* are very similar to those found on the lava-streams of 1872, and described by Scacchi, and to those that can be collected from the surface of other *aa* lavas. They may be classified as follows :—

A.—Scoria, etc., of the actual flow itself, that has become re-involved in the fluid rock.

B.—Pieces of scoria, or lava, from earlier streams, over which the new one has flowed.

C.—Fragments of rock, masonry, or any extraneous solids, picked up from the surface over which the lava flows.

D.—Fragments caught in the passage of the lava through the lateral outlet.

E.—Extraneous pieces detached from the walls of the volcanic canal or chimney.

F.—Materials fallen in from the upper unoccupied part of the vent, and churned up in the lava beneath before it flowed out.

G.—Masses ejected by the explosions, that fall upon a flowing lava.

H.—Accretions in the magma itself ?

It will be seen that there are many sources from which the nuclei of these dumplings may be derived; but in many cases it is not possible to say by which particular means they found their way into the flowing lava. As a general principle, the more complete the adhering crust, and the more fused and altered by heat the nucleus appears, the more likely is the origin to have been one in the interior of the volcano. With regard to section H, most of these supposed accretions are really only parts of the magma that has consolidated at great depths, and been again broken up and swept along by the more recent fluid magma. Others of this category are but very intensely metamorphosed materials, that are tending rapidly to acquire the same composition as the enveloping medium.

The longer and more deeply seated the envelopment, the less are they likely to have a separate crust, or to float to the top as a component of the scum or dross of a lava-flow. The second stage of an enclosure in the magma is one of digestion of the former by the latter. They then more frequently appear as an enclosure of the lava-stream, with, as seen in section, an areola around them somewhat different in colour from the general matrix, and in which areola the

distribution of the phenocrysts and microliths is different. In fact, it is those differences that make the areola visible. In the most extreme case this areola does not exist from its refusion after its first formation.

The most striking examples that prove my original explanation of the origin of these bodies were some of these bombs or dumplings containing masonry. In fig. 18, Pl. XII., we have a very large bomb on the lava some half-way between Boscotrecase and Torre Annunziata, which contained a piece of a wall with a well-formed adherent crust of lava. Most of this cracked off when the dumpling was struck with my hammer; but it is very clearly seen in the photograph, especially on the top and to the reader's left side.

Petrographical and Chemical Characters of the Lavas.—The lavas (figs. 22, 23, 24, 25, Pl. XVII.) are of a very common type of those ejected from Vesuvius during the last two or three centuries, and would be almost indistinguishable from a good many. In clean section they are bluish-grey, fairly uniform in texture, exhibiting scattered augites of bottle-green colour, and sparsely scattered crystals, and crystal groups of leucite. The augites range up to 5 mm. or more in length; but the most conspicuous are from 3 to 5 mm. The diameter of the leucites is about the same. These last have that peculiar greasy, glassy-grey lustre of the fresh mineral, so that they are not easily distinguishable in colour from the matrix. In fact, it is only in old lavas that leucites look more prominent, when the first traces of kaolization begin to give them a whiter colour. Here and there it is possible to pick out an olivine or biotite crystal, so that these are not so common as in many Vesuvian lavas. Other minerals can occasionally be met with, visible to the eye, but can only be considered as accidental constituents of the rock.*

Where quarrying operations have in a few places opened up the massive part of a flow, it appears as a fairly compact and uniform rock, and, no doubt, in the future will take a fair place for industrial uses. In some spots it is of course fairly vesicular. In the cavities of the vesicles, and in the spaces left along the shear planes of flow, an extremely fine geodic lining has been deposited. The crystals are so extremely small, that they are practically incapable of being scraped off. By comparison, however, with the cavity linings of other Vesuvian lavas, I think we can refer them chiefly to sodalite and neochrysolite, fayalite, and probably a little breislakite.

On microscopical examination the augites are seen to be well-formed crystals, with sharp edges, very clean, and containing the usual apatite microliths, and a few well-formed crystals of iron ore. These augites seem to be of two tints, though

* I do not propose to describe here the already well-known petrographical details of Vesuvian lavas in general, and reference is made only to those variations that afford some association with the dynamic manifestations of the recent events at Vesuvius.

in thin section both are very pale bottle-green in colour. The leucites are large, composite, clean crystals, with very few enclosures, at any rate in the larger ones. The augites and leucites are, as very frequently happens, intergrown, though the augite seems to have started individualizing earlier than the leucite. The pectinoid polarization of the leucite is only moderately marked in the interior of the stream, but exhibits more contrast of light and shade near the rapidly cooled surface, or that suddenly cooled by falling into a cistern of water at Boscotrecase. A few olivines or biotites are occasionally met with; in fact, I feel inclined to consider the amount of this latter mineral somewhat above the average for Vesuvian lavas of recent dates.

The matrix consists of a closely packed mass of small leucite crystals fairly well defined, showing usually one or more rings of enclosures, but otherwise limpid. These are enveloped in a thick network of felspar and augite microliths, with small magnetite grains, but no magnetite dust, so that sections are fairly transparent. In the sections taken from the interior of the stream, most of the residual glass seems to have been completely individualized.

What strikes one is the fair uniformity in the limit of size of the post-eruptive leucites. There are a certain number of crystals and crystal groups of all inter- mediate sizes, but the frequency of their occurrence is relatively small. (See figs. 22, 23, 24, 25, Pl. XVII.).

Another point is the relatively small size and unimportance of the felspars. A general glance at the ground-mass impresses one with the fact that the vast number of *small leucites constitutes the dominant constituent* of it.

I thought it wise to compare these new lavas with those produced under different conditions, in the slow and steady outpours that built up the great lava cone of the Colle Umberto. Materials were collected from one of the latest out- flows on the western slope of the Colle Umberto, and therefore emitted about 1899. A section of the interior of this stream (figs. 20 and 21, Pl. XVII.) shows the larger leucites to be very similar to those of the lava of April, 1906, but they grade down to quite the smallest leucite, so that there is no marked character either in size or otherwise to differentiate between the intra- and extra-terrestrial individualization of this mineral. A further more striking fact is, that the vast number of *small felspars constitutes the dominant constituent* of the ground-mass of 1895–1899. The magnetite grains in the 1899 lava are also larger, and, as far as one can see under high powers, are more perfectly shaped.

These somewhat striking differences are quite capable of interpretation. For four years lava remained in the chimney of Vesuvius, from 1895 to 1899, in a comparatively quiescent condition, steadily rising along the main canal of the volcano, and then draining away through a narrow dyke or fissure, until it found its outlet at the summit of the Colle Umberto. For a kilometre and a half

the fluid magma would slowly ooze along a narrow rift, exposed to hardly any mechanical disturbance, partially but slowly cooling under some pressure. The conditions were such as to favour, not the sudden bringing into existence of a great number of leucites, felspar, magnetite, or augite microliths, but the gradual increment of those already in existence. I demonstrated years ago, that the rival minerals leucite and some of the felspars depended for their production on whether there was great or little pressure, and the rapidity of cooling.* Felspars are the slow, more stable, or if I may say so, dignified results of cooling of an igneous rock, whilst the felspathoids represent the more hasty, hurried products. The latter condition was markedly the case with the rapid outpours of lava during the April eruption, although the weeks of cooling of the more homogeneous and bulky lava-streams would partly repair the agitation in the products of the parturient mountain; the vast number of leucite microliths had already been called into existence, each claiming only its limited share of suitable substances for its growth.

We have a striking proof of the large percentage of glass that is differentiated or microlithized in the cooling of these lava-streams at the time of their emission in the following fact : Some of the rapidly flowing lava ran into a deep cistern of water at a villa at Boscotrecase, by which a highly glassy, fragile mass was produced, of a deep-black, vitreous appearance. Under the microscope, the average size of the leucite microliths is smaller (figs. 22 and 23, Pl. XVII.) than in the interior of the lava-stream close at hand, which cooled less rapidly. In the rapidly cooled rock the ground-mass is far more transparent, is largely made up of greenish-buff glass, with the smaller leucite, felspar, and augite microliths much smaller and more sparsely distributed (compare figs. 23 and 25). The iron ore grains are fairly well shaped and, no doubt, represent those already formed before the sudden cooling by the water. This cooling was so rapid that it prevented the ground-mass from becoming dirty and opaque by the liberation of fine magnetite dust, as can be found in the surface of the scoriaceous crust of these same lavas. The microliths are, though very small, very well formed in this glassy ground-mass. Many of the augites show their prismatic, pinacoidal, and domic faces to great perfection, if the focussing screw is kept moving. The lozenge-shaped felspar crystals are equally neat, and quite similar to those described and figured in my account of the 1885 eruption.†

In the following table, we have two analyses of the lava. which are sensibly the same, and quite within the variations in any lava-flow. For the sake of

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* "The Relationship of the Structure of Igneous Rocks to the Conditions of their Formation."— Scient. Proc. Roy. Dublin Soc., vol. v. (N.S.), 1886, pp. 112–156.

† "L' Eruzione del Vesuvio nel 2 Maggio, 1885.—Ann. d. Accad. O. Costa d. Aspiranti Naturalisti Era 3, vol. i., Napoli, 1886, p. 8, with chromolithog.

convenience the other products are also placed in parallel columns, and will be discussed when we come to their description :—

ANALYSES OF LAVAS AND OTHER EJECTA OF VESUVIUS IN APRIL, 1906.

	1. MATTEUCCI, NASINI, CASORIA, AND FIECHTER. Lava of Boscotrecase. Washed and dried at 180°C.	2. LACROIX. Scoria at commencement of paroxysm.	3. LACROIX. Lava of Cognoli, 8 Ap., near cemetery, T. Annuziata.	4. LACROIX. Essential scoria, Ottajano.	5. CASORIA. Grey sand (near Observatory ?). Washed.	6. CASORIA. Reddish sand (near Observatory ?). Washed.
SiO_2	47·644	47·50	48·28	48·10	48·117	48·154
Al_2O_3	18·671	18·59	18·39	15·31	19·082	18·437
Fe_2O_3	3·511	1·52	1·12	3·20	7·709	7·565
FeO	5·854	7·62	7·88	5·45	2·772	2·750
MgO	3·924	3·86	3·72	7·55	3·728	4·432
CaO	8·337	9·16	9·20	12·45	7·949	8·244
Na_2O	2·310	2·72	2·84	1·98	2·528	2·871
K_2O	7·099	7·05	7·25	4·22	6·403	5·834
TiO_2	0·767	1·05	1·28	1·15	undet.	undet.
P_2O_5	0·802	tr.	0·51	0·12	0·852	0·743
H_2O	—	1·25	0·62	0·87	—	—
ZrO_2	—	—	—	—	—	—
BaO	0·177	—	—	—	0·093	0·095
MnO	0·762	—	—	—	0·418	0·394
SrO	—	—	—	—	0·028	0·033
	99·828	100·32	101·09	100·40	99·679	99·552

FRAGMENTARY EJECTA.

Practically no part of the slopes of Vesuvius, or the immediate neighbourhood of the mountain, escaped receiving some of the fragmentary matter shot forth from the volcano. To describe in detail a large number of sections would make this memoir too long; and I have, therefore, endeavoured to give a series, chosen from those regions that received the more important showers of stones and dust, and specially those that illustrate the mechanism of the eruption, or were the

cause of disasters that further knowledge may help to prevent—catastrophes that there is every likelihood will occur in future.

Sections of the fragmentary ejecta deposits around the north and east of Monte Somma, on the main road, upon which are situated the principal towns, are drawn to scale in the diagram, fig. 39. The following were the materials met with, which I give first at their maximum accumulation at Ottajano, extending eastward and south, and then follow with two to the west of Ottajano :—

[The figures in the following sections represent depth in metres.]
(See Plates XX. and XXI.)

OTTAJANO TOWN. *Middle of the Piazza S. Francesco.* (Plate XX.)

(*a*) 0·05 m. of small brownish-black scoria-lapilli, almost wholly *essential ejecta.*

(*b*) 0·15 m. of larger black scoria-lapilli *essential ejecta*, with a red band at junction with last (*accessory ejecta*).

(*c*) 0·49 m. of red lapilli, coarser at the bottom.

Most of this is made up of fragments of ancient lavas and scorias, that composed the old cone-top, and therefore mostly *accessory ejecta.* Scattered sparsely are a few dense scoria fragments, some of which, no doubt, are *essential ejecta* ; but their resemblance to fragments of *accessory* scoria is such as to render them indistinguishable.

(*d*) 0·04 m. of grey dust, mixed with some lapilli like those beneath.

SAN GIUSEPPE D' OTTAJANO. *Close to the station of Circum-Vesuvian Railway.*

(*a*) 0·04 m. fine, brownish-black scoria-lapilli, almost wholly *essential ejecta.*

(*b*) 0·08 m. coarse, black scoria-lapilli of *essential ejecta.*

(*c¹*) 0·17 m. brown to red lapilli, with ejected blocks of altered lava, mostly *accessory ejecta.*

(*c²*) 0·08 m. red and brown lapilli in bands of different coarseness, chiefly *accessory ejecta.*

(*c³*) 0·08 m. coarser lapilli, passing up into finer, also chiefly *accessory ejecta.*

(*c⁴*) 0·02 m. much smaller lapilli of same kind.

(*d*) 0·04 m. greyish dust.

CASILI. *North and towards Ottajano.*

(*a*) 0·04 m. fine brownish-black scoria-lapilli, almost wholly *essential ejecta.*

(*b*) 0·08 m. coarse, black scoria-lapilli of *essential ejecta.*

(*c*) 0·39 m. red and brown lapilli of different coarseness, chiefly *accessory ejecta.*

(*d*) 0·035 m. of greyish dust.

Casili. *South, and towards Terzigno.*

(*a*) 0·04 m. fine, brownish-black scoria-lapilli, almost totally *essential ejecta.*

(*b*) 0.08 m. coarse, black scoria-lapilli of *essential ejecta.*

(*c*) 0·20 m. red and brown lapilli of different coarseness, chiefly *accessory ejecta.*

(*d*) 0·03 m. of greyish dust.

Terzigno. (*South of*) *in a quarry at Caposecchi.*

The three elements of the deposit are similar to those above recorded. The total amounts to about 0·12 m., but the accurate measurement of each component is obviously approximative.

Lagno del Purgatorio, *right or west bank just above main road, west of Somma-Vesuviana.*

(*a* and *b*) 0·015 m. black sand, chiefly small fragments of *essential scoria.*

(*c*) 0·05 m. red, minute lapilli. *Accessory ejecta.*

(*d*¹) 0·012 m. red dust. *Accessory ejecta.*

(*d*²) 0·015 m. grey dust. *Accessory ejecta.*

Lagno S. Patrizio, *just above main road to the east of Sta. Anastasia.*

(*a* and *b*) 0·01 m. black sand. *Essential ejecta.*

(*c*) 0·02 m. red dust. *Accessory ejecta.*

(*d*) 0·015 m. purple-grey dust. *Accessory ejecta.*

The variations in thickness, as the distance increases or decreases from the eruptive centre, are very marked. Thus at Ottajano, above the town, near the Castello, the entire thickness attained 1·20 m. at the P. S. Francesco, in the middle of the town, as above detailed, 0·76 m., and at the lower extremity of the town only 0·55 to 0·60 m., yet this last is only one kilometre farther from the eruptive axis.

At Ottajano and its neighbourhood, in the sections of the final dust-shower, very little difference is shown in the colour at that place, and in the sections to the east and south of that locality ; but immediately to the west and south-west, we find the dust, as at the Vallone del Purgatorio and Vallone S. Patrizio, markedly divided into two beds, one reddish or cocoa-coloured, emitted at an earlier period, and a light-grey in the final phase of the output from the crater. In another series of sections, taken in an oblique manner, cutting off, as it were, the north-west quadrant of the volcano, we shall see how these two elements formed the main constituents of the fragmentary ejecta on that side. I look upon

these two dust-bands at the two localities just referred to as the equivalents of the two dust-beds to the west of the volcano, and, in fact, they can be traced as those equivalents. These sections, however, are types that I chose amongst a great number of others that I examined, which showed that the red or cocoa-coloured dust was, in fact, the more comminuted equivalent of the showers of red-brown *accessory ejecta* (C.) of the sections between Ottajano and S. Casili. It would, perhaps, have been more correct, therefore, to include them in that division shown in the diagram of the sections Purgatorio and San Patrizio.

Punta del Nasone, Monte-Somma. (Plate XXI.)

(*a*) 0·05 m. roundish, brownish-black scoria-lapilli, almost wholly *essential scoria.*

(*b*) 0·12 m. black scoria-lapilli. *Essential ejecta.*

(*c*) 0·40 m. chocolate-coloured lapilli, banded, coarser, and finer. *Accessory ejecta.*

(*d*) 0·10 m. grey dust (after the 13th April). *Accessory ejecta.*

Atrio del Cavallo *between the cone and the Colle Umberto.*

(*a, b,* and *c*[1]) 0·15 m. cocoa-coloured, pisolitic dust, with lapilli more to the bottom. These lapilli, attaining the size of a hen's egg or larger, were chiefly *accessory ejecta,* consisting of old cone components, and rarely a piece of scoria with sufficient of the characters of *essential ejecta.*

(*c*[2]) 0.15 m. cocoa-coloured dust. *Accessory ejecta.*

(*d*) 0·15 m. grey, pisolitic dust. *Accessory ejecta* (after April 13th).

Cancello di Cook, *on the Salvatore ridge.*

(*a, b*) 1 cm. black sand, which could be distinguished as consisting of two layers. *Essential ejecta?*

(*c*[1]) 0·09 m. of grey dust. *Essential ejecta?*

(*c*[2]) 0·05 m. of cocoa-coloured dust. *Accessory ejecta.*

(*d*) 0·05 ? whitish-grey dust, much drifted by the wind, and, therefore, of a variable and uncertain thickness. *Accessory ejecta* (after April 13th).

Eremo, *close to the Observatory, on a well-sheltered, flat roof.*

(*a* and *b*) 0·01 m. of coarse sand or small lapilli, the lower half more compact, the top looser. *Essential ejecta?*

(*c*) 0·10 m. grey pisolitic dust. *Essential ejecta.*

(*c*[2]) 0·13 m. stratified cocoa-coloured dust. *Accessory ejecta.*

(*d*) 0·3 m. grey dust. *Accessory ejecta* (after April 13th).

* I have some doubt whether the bottom black sand is not the same as that which fell in Naples in the first days of the eruption.

As we approach the cone, the thickness of fragmentary ejecta rapidly increases; but the different disturbing influences were so great that little can be learned by excavating sections of the deposits. Vast quantities of ejecta that collected on the outer slopes of the cone continually slipped down as great avalanches sweeping out over the Atrio, mixing their debris with that on the spot where the moving masses come to rest, and so destroying any order of stratification. We shall more fully enter into this subject when describing the changes of the great cone.

If we select a number of pieces of the lower and first *essential ejecta*, we find them composed of a fairly light, spongy scoria, with a faint tendency to pumiceous structure. Their volume varies according to the distance from the eruptive axis, but at Ottajano pieces up to the size of a pigeon's egg were common. As I pointed out years ago, the size and density increase as we approach the eruptive centre in the azimuth of the shower. At Ottajano, a small proportion of the large pieces will float in water. Were it necessary to make a bulk analysis, it would be requisite to collect specimens from the whole line of fall, and take an average from these.

Projecting into the cavities of the scoria, we can occasionally see a nearly free crystal of augite, of leucite, and rarer of olivine and mica.

The making of microscopic sections is a difficult task, as in all vesicular rocks; further, the opacity is so great in this case that the grinding must be carried to extreme thinness to render them sufficiently transparent. Fig. 26, Pl. XVIII., gives a representation of the appearance when magnified $17\frac{1}{2}$ diameters. The vesicular structure is characteristically that of a scoria and not a pumice. A very large proportion of this scoria is composed of a buff or faintly greenish glass, scattered throughout which are large numbers of porphyrite leucites, augites, and the other usual mineral components of Vesuvian *essential ejecta*, fragmentary or otherwise. There is nothing very special about any of these, except that most of the larger augites are much more crowded with glass cavities than the lavas. They are darker bottle-green in tint, and zoned, and also polarize in brilliant and variegated colours from irregular and rapid cooling, independent of these zones. There are also some light augites like those in the lava. The larger leucites are remarkably clear, and polarize rather strongly, such as would be expected with the rapid cooling of the scoria. The medium and smaller-sized leucites, down to the very minute ones, exhibit neat, well-formed trapezohedrons, that are well seen in the patches of clearer glass by the constant use of the focussing screw. With higher powers (fig. 27) beautifully formed microliths of great minuteness can be seen as completely crystallized as those we can collect half a centimetre in length. Of course, they are too small to show any appreciable polarization. Numbers of other rod-like microliths are probably the felspars; but here there is no recognizable

crystalline form; nor do they sufficiently polarize to enable us to determine their nature : hence we can only judge of their constitution by analogy. A few are in the beautifully neat diamond-like plates, such as I described in the 1885 lava, and considered as felspars. In some spots the glass is absolutely devoid of iron ore microliths ; but in others, more or less abundantly, may be seen dark-brown crystallites which, also by analogy, we refer to that mineral.

We glean from examining this scoria, that the magma from which it was derived was composed in very considerable part of a glass fairly charged with H_2O* in solution, acquired in the higher, though not the top, part of the volcanic chimney. As soon as the great plug of lava above it had rapidly been removed, as a cork from a lemonade-bottle, it frothed and scummed up by the rapid escape in a gasified form of its dissolved H_2O, accompanied, of course, by an enormous explosive power, and, above all, by a rapid loss of heat-energy requisite for that gasification or vesiculation. No time was allowed for much further individualization before the glass set.

Deeper down in the volcanic chimney was other magma, which had less opportunities for acquiring H_2O. This rose, following that portion of the magma that supplied scoria (*a*), and was ejected, constituting the black scoria-lapilli (*b*). Macroscopically, it much resembles its eruptive predecessor, but is denser, always sinking in water ; it is blacker, and the average size of the vesicles is smaller. Compare figs. 26 with 28, and 27 with 29. Even in the very thinnest section that human ingenuity can prepare, it appears microscopically as a jet-black network (fig. 26), with here and there near the edges of the slice a fortuitous, almost infinitesimally thin, wedge-like edge, just penetrable by a very powerful light from the sub-stage. Such a spot is photographed in fig. 29. It differs from the first ejected scoria (*a*) by the glass being choked by vast numbers of augite, possibly felspar, microliths, and iron-ore dust. To this latter is especially due the intense black opacity of this scoria.

Being a less gas-bearing magma, its cooling was slower, and consequently time was given for the more extensive though hasty individualization of the potentially existing minerals.

Essential ejecta—which, no doubt, did to a small extent quit the throat of the volcano during the production of the red and brown lapilli-beds and the chocolate dust—are very difficult to recognize, on account of their acquiring an old look from attrition with the other lapilli. They are then indistinguishable from scorias of earlier eruptions that in part constitute these *accessory ejecta*. By carefully selecting pieces from some of the Atrio sections, close to the foot of the cone, but just beyond the reach of the slips of loose ejecta, I was able to recognize the

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* I always use the formula, not to denote any special physical state of the substance.

ejecta as masses ranging from the size of a walnut up to that of a man's head or larger, with a hardened denser surface, showing slight bread-crust structure. The material is a dense black or purple-brown pumiceous scoria, rich in phenocrysts of augite, leucite, and other essential minerals, and often extraneous fragments, with which, no doubt, it was churned.

In structure the material has a much finer vesicular structure, as seen in fig. 30; but its blackness from pulverulent magnetite in the matrix of the mass is most marked. The phenocrysts are the same as those of its two predecessors; but I think there are perhaps more mica crystals, though this may be due to the diminished bulk from the smaller vesicles, and therefore the greater crowding of all the porphyritic crystals. There also seems to be more microlitic devitrification of the glassy base.

A comparison of the size and number of vesicles in sections (figs. 26, 28, and 30, Pl. XVIII., or, again, figs. 27 and 29) shows that as the magma rose from greater depths it was less and less rich in water.

These words had already been written when I received the memoir of Prof. Lacroix, in which he gives an analysis of these scoriæ, comparing the figures with those of the lava. No mention is made as to which band they were derived from, and no precautions appear to have been taken to average samples from a long stretch of country over which they fell.

From this analysis Lacroix concludes that the magma that produced this pumice was different from that which flowed as a lava; and it is given one of the new rock names. Had the precautions mentioned above been taken, or had due credit been given to aerial sorting of fragmentary ejecta, I think that the author would not have come to such conclusions. I have over and over again shown how the alkalies are modified in quantity in different parts of the contents of an open volcanic chimney. By such change of conditions, we have more than sufficient explanation found in a single lava-stream. Above all, I must enter a protest against the injury to true science by the use of excessive nomenclature that hides facts, confuses our thoughts, and misleads our investigations.* It is irrational for different names to be given to the crust of lava, to portions of it that fall into a well, to the material that cooled in its main mass, or again to other portions of the same magma ejected as fragments, because the vapour contents were greater.†

We have other analyses showing that associated with the insoluble part of the lava and scoria there is a considerable proportion of soluble salts; but the analysis given by Lacroix makes no mention of these as to whether they are estimated in the bulk analysis or not.

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* " Etude Minéralogique des Produits silicatés de l'Eruption du Vésuve (Avril, 1906)," &c.—Nouvelles Archives du Museum, 4 série, tome ix., p. 28.

† *Op. cit.*, p. 151.

Casoria* found soluble salts in the cocoa-coloured dust equalling 3·219 per cent., and in the grey dust 2·626 per cent.

Surely, the amount of soluble saline contents of the lava must vary according to the number and size of fissures, by which some of these substances could have volatilized off. To repeat what I stated in detail twenty years ago, the composition of a magma in the upper part of the chimney of a volcano, over and above any effects due to osmosis or diffusion from the walls of the canal, will vary more or less through the loss of some of its own more volatile constituents. If a column of lava has been in a state of ebullition for months in the upper part of the open volcanic chimney, surely there will be a much larger amount of alkalies *fixed* in the solid and insoluble part of the resultant rock, representing the bases retained in the magma, whilst the acids have escaped as HCl, SO_3, HF, &c., in the vast volumes of the smoke continuously evolved from the volcano. In a lava-stream undergoing slow cooling we have the sublimation of chlorides and sulphates in abundance, as probably the temperature is too low for SiO_2 to drive out the HCl, SO_3, &c., in the alkaline chlorides and sulphates.†

Not unlikely, the rapid evolution of H_2O in the *essential magma* of the paroxysmal or explosive phase of eruption will carry with it the chlorides, sulphates, &c., as such. The purging of the magma is so rapid, and the coincident cooling also, that no time is given to the SiO_2 to perform its function as it would do in a mass of magma undergoing slow cooling at a high temperature.

I do not attribute the differences in composition between the lava and the essential scoria to any one of these causes; but I do maintain that until we have a very extensive and detailed investigation of this point, we have no right to generalize on a slight increase or diminution of alkalies in the products of different phases of activity of a volcano, or to increase a superfluous nomenclature on such slight variation of composition. Still more is this the case when, as pointed out above, due credit has not been given to aerial sorting in showers of fragmentary ejecta, or a definite estimate of the soluble and insoluble components in an analysis.

The dusts, either grey or chocolate-coloured, are composed of fragments of the usual mineral constituents of lavas and scoriæ of Vesuvius, and represent the triturated components of the summit and heart of the great cone, which was removed by this eruption. Chemically, as shown by the analysis at p. 166,

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* "Sulla Composizione Chimica delle Cenere Vesuviane cadute a Portici nei Giorni 9 e 10 Aprile, 1906." Portici, Della Torre, 1906.

† Recently M. Albert Brun has made some interesting studies ("Quelques Recherches sur le Volcanisme."—Arch. des Sc. Phys. et Nat. de Genève, Mai, Juin, 1905, et Nov., 1906) on the volatile components of volcanic products; and though I do not accept many of his conclusions, still there is much of value in his researches. His laboratory researches for volatile elements in lavas refer, to my mind, only to the rarer, less detachable, and therefore residual substances.

the composition is sensibly the same as that of the newest lava, except that the iron is more peroxidized; exactly what we should expect. The differences between the insoluble constituents of the two-coloured dust are only nominal. When we examine, however, the soluble saline part, we find that the salts of the cocoa-coloured dust contain 4 per cent. more Na, but $2\frac{1}{2}$ per cent. less K, than the grey dust. Ca also is more than 1 per cent. less in the red than the grey dust, whereas the former is poorer in SO_4 and richer in Cl.

As will be seen by the appended analyses,* the salts of the new lava are very different in composition from those of the dusts. Carbonates predominate in the lava, and chloride in the dusts.

	HCl.	H_2SO_4.
100 grammes of grey dust contain . . .	0·00219	0·00294
100 grammes of cocoa-coloured dust contain .	0·00109	0·00145.

Only the faintest traces of sulphurous acid were found.

Hypothetical Salt Grouping.	In Red Dust.	In Grey Dust.
NaCl . . .	49·158	44·300
$MgCl_2$ . . .	5·110	6·964
$MnCl_2$ . . .	1·494	1·559
$CaSO_4$ . . .	27·198	31·731
K_2SO_4 . . .	8·399	13·488
Na_2SO_4 . .	8·557	1·927
SiO_2 . . .	0·079	0·026
Total .	99·995	99·995

	Red Dust.	Grey Dust.	Sol. Salts in Lava of Boscotrecase.
Ca . . .	8·399	9·334	0·945
Mg . . .	1·292	1·759	—
K . . .	3·768	6·048	12·758
Na . . .	22·116	18·047	30·395
Mn . . .	0·657	0·681	—
Cl . . .	34·520	32·977	20·136
SO_4 . . .	29·520	31·150	4·723
SiO_2 . . .	0·079	0·026	—
CO_3 . . .	—	—	30·749
Total .	100·351	100·022	99·995

Dried at 180° C., the red dust contained   .   .   .   . 3·240 per cent. of salts.

,,   ,,   the grey dust contained   .   .   .   . 2·651   ,,   ,,

,,   ,,   the lava of Boscotrecase contained   .   . 0·395   ,,   ,,

These salts are probably derived from sublimates in the interstices and fissures of the cone, which a careful observer may watch continually being deposited from the escaping vapours of the magma occupying the chimney. In fact, this saline constituent represents the pulverized remains of the halite, sylvite, erythrosiderite,

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* Casoria, Prof. E., *op. cit.*

chloromanganokalite, apthitalite, gypsum, and other minerals of this class, which, we shall see, were ejected in a state still unpulverized at the same time. It is probably the presence of a little free acid that has changed the red peroxide of iron, making the colours differ. In fact, as seen in the table, Casoria found these dusts to contain free acid, which he determined as double in the grey dust, compared with that in the red dust.

During the suspension in the atmosphere of these dusts, small local showers or rain-drops fell, and produced at certain spots great numbers of pisolites. These, though very small, exhibit all the characters of those I described in the Plinian dusts and other similar ones ;* that is, there is a minute central cavity formed by the jamming together and arching of the first coarse particles caught by the rain-drop. Around the coarser-grained nucleus come layers of finer and finer material, as the available water for wetting got scarcer, so that, at the surface, it was only the most impalpable powder that could adhere.

The thin stratum of black sand at the base of the deposit at Cancello di Cook, and the Eremo, although shown in section as *a* and *b*, represents a good deal of fine *accessory* or even *essential* material also, which could reach these localities quite early in the eruption, probably corresponding, as I have already said, to the first ejection of black sand that fell in Naples on the evening of the 4th of April.

Prof. Semola, of the R. Observatory of Capodimonte, found that the black sand that fell there on April 4th, 5th, and 6th weighed 1170 grammes per litre or decimetre cube, that is, in bulk slightly heavier than water. The reddish dust of the following days he found weighed 0·880 grammes per decim. c., or in bulk lighter than water. Casoria† gives the specific gravity of the grey dust of the 4th, 5th, and 6th as 2·7159, and that of the cocoa-coloured dust 2·7706 ; but his was collected much nearer the eruptive centre.

The Cone and its Modifications.

The dominant features of the eruption of April, 1906, of Vesuvius were the extensive truncation of the great cone, and the large amount of fragmentary ejecta spread over the mountain and region around Vesuvius. If we go back over a century, we can give many examples of as extensive outflows of lava, but we find that the only parallel for paroxysmal energy and degradation of the cone is that of 1822.

From whatever aspect an observer looked at Vesuvius for many years before the recent eruption, the striking characteristic of it was the symmetrical form of the great cone, only broken here and there by the humps on the S. S. W. and S. E. slopes. These were most apparent as interfering with the symmetry when the

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* " Geology of Monte Somma and Vesuvius."—Quart. Journ. Geol. Soc., vol. xl., 1884, p. 83.

† *Op. cit.*

mountain was viewed from the south between Torre del Greco and Torre Annunziata (fig. 10, Pl. X.). On approaching and inspecting the great cone from the Pedimentina, the Atrio del' Cavallo, or the ridge of Somma, one was impressed by the relative smoothness of its surface. This was due to the practical absence of any water-erosion on the extremely permeable coarse lapilli, scoriæ, or thin scoriaceous lava-surfaces that clothed it, and any gutter or irregularities of it were soon obliterated by the shifting, unstable nature of its covering, so that depressions were rapidly filled up, preventing water from collecting in mass.

The principal cause of its smoothness was, however, the absence for many years of any important fall of fine dust in sufficient quantities to make an impermeable surface upon which water could be collected, in sufficient volume, and be shed so as to produce erosive action.

When the huge, sombre dust-screen disappeared after the eruption, the remains of the great cone offered to the eye a view of its slopes deeply scored by a series of remarkable symmetrically arranged *barancos* of no mean dimensions, extending radially from the crater-edge (Pl. V.). The first explanation that suggested itself was water as the sculptor of these; but when it was known that only relatively insignificant showers had fallen during and immediately after the eruption, it was patent that other causes had been at work.

On my arrival at Naples, late in April, as I watched the cone day by day, I was struck by the almost continuous slips that were taking place on its flanks; and by carefully watching them, it could be seen that these masses of loose material were practically identical with snow-avalanches. I attempted to photograph some of these; but unfortunately the negatives turned out unsatisfactory. Two photographs, however, were more successful—by M. F. A. Peret and M. A. Brun—one of which I am able to produce here by the courtesy of the artist (Pl. XIX.).

The new crater-forming stage started on the 4th of April. As the magma sank in the chimney, in consequence of the new drain opened to the south, the ejection of *essential materials*, as lava-cakes in the cone-forming stage, gradually ceased, and during the afternoon were mostly replaced by the *accessory materials* derived from the now unsupported chimney-walls. During the next three days a thick layer of the debris of the now rapidly growing crater was spread over the slopes of the great cone and its immediate neighbourhood. During the great output of fragmentary materials from the 7th to the 9th vast quantities must have been spread as a heavy mantle on the cone, and, no doubt, a good deal of slipping then occurred. During the very violent propulsion of the fragmentary debris of the rapidly growing crater, much of it reached beyond the slopes of the cone. Later, as the ballistic energy of the volcano diminished, and as materials had to be hoisted from greater and greater depths, as the crater-apex was lowered, the

ejecta would reach lesser and lesser distances. At the same time, more hot and dry dust would be mixed with the coarser materials, rendering their repose on an incline more and more unstable. The mountain would then be sheathed in a thick mantle of a loose, incoherent collection of blocks and masses of different size, ranging down to flour-like dust. As the propulsive energy still further diminished, the fragmentary materials would only just fall without the crater-rim. Gradually the increasing pile of materials on the outer-lip of the crater would reach the limit of stable equilibrium, and would begin to slide down, starting other materials below them, so that the moving mass would rapidly acquire increased volume and momentum, and would sweep down, ploughing out a ravine just as a snow-avalanche does. This, no doubt, occurred again and again, all round the crater-rim, until the whole mountain-slopes were scored into ridges and furrows.

The mechanism may be seen in an ordinary heap of dry sand; but by mixing any fine, light powder with different-sized dry gravel on a slope of about 27°, the process may be imitated to perfection.

The gigantic size of many of the blocks ejected may have frequently been individually sufficient to have initiated the starting-point of a big slip. Such a mass as that seen in fig. 3, Pl. VII., and which weighs *at least* 30 tons, has travelled over a kilometre from the crater, and denotes a very powerful impulse to have sent it so far with the high trajectory necessary to propel it from the crater-bottom. Had it pitched on the crater-edge, we can quite comprehend what a powerful initiator of an avalanche it would have been, not to speak of its function as a plough. The force with which projectiles struck the surface of the cone is witnessed by the pieces of metal gouged out of the steel-rails that remain of the funicular railways.

In my first attempts to reach the crater after the eruption, the ascent along one of these barranco bottoms was most instructive. It required all the skill and nerve of an experienced mountaineer to avoid converting oneself into the starter of an avalanche of stones, in which one stood of course every chance of being overwhelmed. Minor slips constantly occurred every few paces, and others were progressing in the neighbouring ravines.

No doubt, in the period of great volcanic activity, the continuous quaking and tremor of the whole mountain must have vastly helped the shaking down of the unstable material from its slopes. In addition, the great pseudo-fluidity of fine dust, when very dry, is known to everybody. The powdered rock, mixed with coarser materials, acted the part of a solid lubricant, just as talc or plumbago-powder would of course do in a greater or less degree.

Furthermore, all was at a very high temperature, and the convection air-current set up around each particle would diminish its effective weight, and

tend to raise it.   In addition to these influences, the hot air and gases escaping from the mountain side all tended to prevent materials adhering to it.   I found at the end of April, 200° C. in the material of the south-west lip of the crater, that part in fact the most exposed to rapid loss of heat.

Naturally the greatest thickness of these breccias is in the quadrant between the north and east of the mountain, where in a few hours ravines have been cut out that impress one as having required centuries to be eroded.   In the photograph (Pl. VI.) the lower terminations of two of these are shown.   The maximum depth must exceed 30 m.; and if the new map (Pl. XXIII.) is compared with the old in some places, the addition must attain 50 m., where the much more acute angle between the base of the old cone and the Atrio existed.   There were several spots where I was able to measure the height of the sides at over 20 m., and where there must have been quite another 10 m. below the barranco floor at the same spot.

On the north-west and west (Pl. III.), and also on the north-east and east sides of the mountain, there are still thick mantles of ejecta covering the cone; but on the north and south sides much of the loose materials have slipped down.   Even on the south-west side, near the site of the old funicular railway, most of the materials have slid down.   It was due to this that the major part of the railway was wiped, as it were, from off the mountain-side.

The avalanche at this part was terrific in its destructive effects.   It stripped off the upper two-thirds of the railway, cleared away the great water reservoirs, the restaurant, the station, boiler and machine-house, and stables, not leaving a trace of any of these.   The last zigzag part of the electric tram-line was swept away down the mountain; the rails, hanging together by the fish-plates, formed long strips of twisted iron, stretching radially to the mountain, instead of in their original position tangentially to it.   The remains of the cable, rolled up like a tangled ball of string, lay about a kilometre away on the Pedimentina; the two boilers, also several hundreds of metres below the site of the old boiler-house (figs. 4 and 5, Pl. VIII.).   Scattered about were twisted and contorted rails, trolley-poles, wires, and other debris, projecting here and there from the chaotic jumble of rubble.

All the higher *bocche* that emitted the lavas are entirely covered by great avalanches of debris, some of which had power enough almost to reach in places the edge of the Pedimentina.   The extreme rending of the cone by the different radial dykes on the south side brought about a great deal of slipping of the older materials on that aspect of the cone, and there one may see some irregular couloirs, differing from the others in being branched.   The quaquaversal structure of the cone has favoured the peeling off and slipping of a very considerable thickness. The process continued for months after the eruption, and was still in progress

in November, when I examined the locality. It was steadily extending upwards, and would soon reach the edge of the crater, so that in future the cone will here possess a marked depression, and consequent weakness, in the direction favourable for future outbursts. No doubt, the number of new dykes will tend to knit the cone together in that direction, which will in some way compensate for the loss of material on the south side.

The angle between the Pedimentina and the cone on the south was a fairly sharp one before the eruption; but the vast amount of material of the slips has filled it up, so that it is almost impossible to draw a line between cone and Pedimentina.

Before the eruption the Colle Margherita stood out as a distinctive feature in the Atrio del Cavallo; in fact, it formed a third though smaller prominence between the summits of Somma and Vesuvius. Between the cone and the apex of the Colle Margherita there was a distinct notch. Since the eruption that notch has been filled in, so that one walks almost on a level from the slope of the cone along a blunt ridge or saddle to the summit of the Colle Margherita.

The cone, before the eruption, was a fairly symmetrical one, even at its summit. The constant activity of Vesuvius from 1876 had steadily filled up and healed, as it were, the crater of 1872, and had piled up on the materials filling that crater other lavas and scoriæ, so that the apex of the eruptive cone, although somewhat blunt, formed a fairly harmonious curve with the sloping sides of the great cone of Vesuvius.

The exact altitude of the cone during the days preceding the eruption is rather difficult to fix, as it varies from day to day. Calculating from A. Fiechter's data* and the new map issued by the Istituto Geografico Militare, the result of their survey, the height works out at 1323 m. or 1330 m. Mercalli† gives it at 1335 m., and De Lorenzo‡ puts it at 1321 m. Taking the average of these four, we get in round numbers 1327 m.

In October, 1903, I fortunately took a panoramic view of Vesuvius from the Punta del Nasone; and on May 4th, 1906, just after the eruption, again made another photograph with the same lens and camera, and from the same spot. The latter photograph is reproduced in Pl. III. I have added the outline of the 1903 photograph, which gives an exceedingly clear, graphic conception of the great changes in the shape of Vesuvius. The first point that strikes us is the removal of about one-third of the original cone by the formation of a large crater. I say *large*, as compared with those usually produced by paroxysmal outbursts at Vesuvius; but really very small if we compare it with that of the ancient explosive eruptions of Monte Somma, represented in the same photograph as encircling the whole cone

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* *Op. cit.*, Boll. Soc. Geol. Ital., vol. xxv., p. 846.　　　† *Op. cit.*, p. 17.

‡ Quart. Journ. Geol. Soc., vol. lxii., p. 481.

of Vesuvius, the Atrio del Cavallo, the Val d' Inferno, and the Pedimentina. At the termination of the eruption at the end of April, the new Vesuvian crater was limited by an irregular edge, the western border only approaching horizontality, and giving the cone a symmetrical outline (Pl. III.), which, looked on at that side, was remarkable for a few days after the eruption. On the west, the maximum altitude in the September following was 1223 m. From this point the altitude of the edges steadily fall, so that almost opposite, on the same date, the lowest lip was a little north of east where the height was only 1103 m. Immediately after the eruption in the latter days of April, the lowest point was due north (Pl. IV.). Rapid disintegration was, however, constantly proceeding in the north-east quadrant. Early in May the lowest point was to the north-east. During the summer of 1906 there was a constant crumbling and slipping of the edges, considerably lowering them, and enlarging the diameter of the crater. This occurred mostly in the north-east quadrant, and also to the north-west. The parts that had practically remained undisturbed when I examined the crater early in November were the south-south-west and north lips. This was due to the much larger amount of lavas entering into the structure of the cone at these places ; whereas the north-east side of the cone seemed almost entirely composed of relatively incoherent materials, that were constantly crumbling into the crater.

During the months subsequent to the eruption, not only did the crater increase in the size of its upper opening, but this was continually changing. Still it has maintained up to November, 1906, a fairly circular outline. Signor Fiechter's survey in September shows a maximum diameter N. N. E. to S. S. W. of 720 m., and a minimum diameter in W. S. W. and E. S. E. of 620 m. To be quite correct, it is ovoid in plan, with the larger extremity to the N. N. E.

Various estimates have been given of its depth, all of which are extremely problematical, as it is impossible to get a view of the crater-apex. Towards the end of April, when I was first able to reach the crater-edge, this sloped inward at an angle of 34° for a distance of from 10 to 30 m., and then plunged at an extremely high angle downwards. In consequence of the extreme danger of approaching the friable and unstable edge, and still more of venturing inside, no view was obtainable of the bottom even up to November (Pl. XVI.). Professor Loczy in my company made some trigonometrical observations early in May, and as far as could be reached by the eye, spots on the opposite wall could be fixed at 200 m. in depth. Knowing what I do of the slopes attained in Vesuvian craters, I have no hesitation in saying that at that date it was still quite 400 m. in depth.

The dying efforts of the eruption at the end of April were represented by explosions from the crater-apex, which was situated considerably to the west; and this eccentricity persisted right on to November, as can be seen in fig. 6, Pl. VIII., and Pl. XVI., where the issuing puffs of steam rose up the western wall of the

crater. This eccentricity not improbably marks the actual axis of the volcanic chimney, and has an important bearing upon the oblique truncation of the crater, and the direction of the fragmentary ejecta to the north-east.

The great paroxysm that commenced late on the evening of April 7th, and lasted for twenty-four hours, was characterized by the ejection of a vast amount of fragmentary materials, which, as we have seen, collected on the slopes of the cone, and spread away to the north-east quadrant of the mountain. The sections in Pl. XX. show the chief fall on the road that encircles the north and east of Monte-Somma and joins up the towns there at its base, as being limited by the Lagno del Purgatorio to Terzigno. The cloud of lapilli and dust spread out, extending in a fan-shape over the Campanian Plain, the Apennines, away over the Puglian plains, and the Adriatic coast. Its northern limit passed near Campobasso, and its southern limits would be represented by a line drawn from Vesuvius to Baia. Along the Nola-Bajano railway-line the thickness of fine lapilli reached from 8 to 12 cm.

During the days following the great outburst of fragmentary ejecta, some of the dust even crossed the Adriatic; and later the fall of dust, supposed to be of Vesuvian origin, is reported from Spain, Paris, Berlin, and other places.[*]

The amount of dust spread around the immediate neighbourhood of Vesuvius was very considerable, and depended on the caprice of the winds. Naples was reduced to a filthy state, though the actual depth of dust was not very great. It has been variously estimated at from $\frac{1}{2}$ to 5 centimetres. No doubt, different parts of the town received more or less, as they were sheltered from the wind that was blowing. The amount was, however, sufficient to collect on the roof of the market-house of Montoliveto, and cause it to collapse, killing several people beneath its ruins. This accident, however, is more attributable to the disgracefully neglected condition of the building than to the weight it had to support. Professor Fergola estimated 153 tons of dust per hectare, which equal 15 kg. per square metre. Sabatini[†] quotes Professor O. Fava as finding on his terrace at the Salita Stella in the centre of Naples material that weighed 12 kg. per square metre. As this spot is not far from Montoliveto, we have some idea of the slight weight necessary to crush in the market roof. Professor O. Fava estimated the thickness at 5 mm. It must be remembered that Capodimonte is nearer the north-easterly quadrant, and therefore probably received more and heavier material.

Several explanations have been offered of the distribution of the fragmentary ejecta, almost exclusively limited to the country in the north-east quadrant from

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[*] Dr. Lenand, at Neustadt, after heavy rain and wind that blew on the 14th and 15th from the south, collected, on his verandah, a yellow powder. Prof. Braum, of Kiel, who examined the specimen, found the material very pure, with all the mineral components of the rocks of Vesuvius.

[†] Eruzione Versuviana dell' Aprile, 1906. 2a edizione. Roma, 1907.

Vesuvius.   None are very satisfactory, and each writer has limited his explanation to one theory.   One group of writers attributes it to a strong south-west wind, not having taken the trouble to apply to the neighbouring observatory of Capodimonte for accurate data, which I here append, and for which I must thank the director, Professor Semmola :—

ROYAL OBSERVATORY OF CAPODIMONTE, NAPLES, 1906.

APRIL.	Barometric Pressure reduced to 0° : 700 mm. +				WIND.					
					Direction.			Kilometres per hour.		
	9 a.m.	3 p.m.	9 p.m.	Daily mean.	9 a.m.	3 p.m.	9 p.m.	9 a.m.	3 p.m.	9 p.m.
1	50·0	50·2	52·8	51·00	N.N.W.	N.N.E.	N.E.	17	17	10
2	54·6	53·7	55·3	54·53	N.	N.N.E.	N.N.E.	11	17	10
3	56·1	55·8	57·0	56·30	N.N.E.	N.N.E.	N.E.	28	22	24
4	59·5	58·7	59·5	59·23	N.E.	N.E.	N.E.	15	19	17
5	58·4	56·6	56·4	57·13	N.	N.N.E.	S.	10	4	5
6	55·1	54·2	54·4	54·57	N.	N.N.E.	N.N.E.	12	13	13
7	53·3	52·5	53·3	53·03	N.N.E.	N.E.	N.N.E.	17	20	16
8	51·0	48·4	48·3	49·23	N.N.E.	N.N.E.	N.N.E.	17	20	18
9	48·2	47·7	49·7	48·53	N.N.E.	N.E.	N.N.E.	18	16	14
10	50·8	51·7	54·0	52·17	N.N.E.	N.E.	N.N.E.	16	20	12
11	56·9	56·7	57·4	57·00	N.	S.W.	N.N.W.	7	15	8
12	57·1	55·5	55·7	56·10	N.N.W.	S.	N.	3	6	9

PROFESSOR SEMMOLA.

From this we glean that from the evening of the 7th till the evening of the 9th a steady wind was blowing from the N. N. E. at the rate of from sixteen to twenty kilometres per hour.   That this wind did exist in Ottajano is proved by the peculiar round holes and cracks in the glass windows, described by Profs. Bassani and Galdieri, and others, being limited to that aspect of the houses. Prof. W. Herbert Hobbs [*] explains this by the inrushing vorticose current around the rising column of hot gases.   Others attribute this peculiar distribution of the ejecta to an oblique projection from the mountain, as this has been observed to occur on former occasions.   Such a cause would explain dense fragments of some considerable size reaching, say as far as Ottajano, but would absolutely break down in solving the spreading of finer and finer lapilli and dust miles to

[*] " The Grand Eruption of Vesuvius in 1906."—Journ. Geol., Chicago, Oct.–Nov., vol. xvii., 1906.

the north-east in face of wind blowing from that quarter. No reason is given in some cases for this oblique line of projection; but other writers attribute it to the lower truncation of the cone on the north-east side. It seems to me that the effect is taken by them for the cause. Even admitting that this difference in level of the crater-rim did have some influence, it would be out of all proportion to the remarkable limitation in the distribution of the ejecta.

Various estimates are given as to the height that the uprising column of ejecta reached—

Bassani and Galdieri put it at			4000 m.
Luigi Conforti	„	„	4000 m.
De Lorenzo	„	„	7000 m.
Lacroix	„	„	4000 m.
Matteucci	„	„	10 to 13000 m.
Mercalli	„	„	4 to 5000 m.

If we take 5000 m. as a fair average, it is hardly credible that the energy necessary to raise the fragmentary materials to that height could be much influenced by the relatively small difference in the level between one side of the crater and the other, which we might at that moment estimate to be under 100 m.

When I visited the crater, at the end of the eruption, the escape of the final puffs of dust and sand was occurring close to the west wall, but whether more to the north or to the south it was impossible to ascertain. I have already explained that the west and south-west parts of the crater-rim were highest in consequence of the larger amount of solid rock entering into their composition, whereas the north-east part was very friable and incoherent. What probably happened was, that the true eruptive axis at the time of the crater-formation was not that of the crater, since erosion took place on one side more easily than on the other. The result of this would be, that the crater-walls, being more resistant on the south-west, would tend to overhang the rent, and be diverted to the north-east, where the inner slope of the crater would be the more marked, and the edge of the crater lower—all favourable to the more easy projection of the loose materials to the north-east.

This projection to the north-east, I repeat, could only be very limited in extent at any distance from the crater; and we have still left the elucidation of the spread of the ejecta far afield to the north-east, in what was supposed to be a contrary wind. Those who observe Vesuvius will frequently perceive a phenomenon well known to meteorologists and aeronauts, namely, currents of air blowing in different directions. One may often notice the " smoke " of Vesuvius trend away in one direction, and, at a height of 500 or even 1000 to 2000 metres, bend over, and be traceable as a dark streak for fifty miles in the opposite direction. At

others it will rise up for 500 or 1000 m., and then, meeting with a strong current, be carried away as a horizontal band in the sky. There is no doubt, I think, that such a strong south-west wind was blowing, although not so near the ground as to be within the reach of the meteorologist's observations, and, therefore, not the imaginary one of De Lorenzo and other writers. This wind swept the ejecta away to the north-east over the whole of Italy in that direction and across the Adriatic. As the stones fell from the upper south-west current into that of the north-east, they must have returned over part of their route. When they reached Ottajano, they struck the window-panes directed to a north-east aspect. Unquestionably, there must have been a tendency for a vorticose inrush of air all round the volcano; but this would obviously be less marked on the side of Somma than on the other unobstructed sides of Vesuvius.

To sum up, we may attribute the peculiar distribution of the scoria to different concurrent influences—(a) Heterogeneous structure of cone, unsymmetrical crater, and oblique projection; (b) two strata of air-currents in opposite directions.

Immediately after the eruption the edges of the crater were so dangerous, and the sides so plastered with the last expiring puffs of dust and sand, that very little could be made out of the structure of the cone. In November the gradual peeling of the walls, helped by some heavy rains, left the surface clean. Many dykes could be distinguished, mostly in the vertical, or nearly vertical, radial orientation; but a few, obviously not lava-streams, were horizontal. I tried, as on former occasions, to photograph with a telephotic lens, but the unstable and dusty state of the atmosphere within the crater prevented the operation from being successful.

In fig. B (A) was a dyke on the north wall of the crater, perhaps some 30 m. from the crater-edge. Its upper limit was hidden by a large volume of steam escaping from its upper canal. It is a most interesting example of the hollow dykes, the nature of which I was the first to describe in referring to the eruption of 1885. The two canals are divided by a floor, and the lower one is nearly filled by loose scoria. This dyke may possibly be that of 1891, and records somewhat the following sequence of events. The dyke was formed and reached the outer surface of the cone; lava flowed through the rift. This went on until most of the fissure was filled by the solidifying rock, only a channel (A^1, A^2, A^3) remaining, where the flow was greatest, and probably just above the level of the outlet on the cone. The lava in the chimney went on draining away, till its surface was reduced below the lateral outlet, and it then stopped, and what remained in the lower part of the rift cooled a crust on its surface between A^1 and A^3. A fresh outlet was formed on the cone at a lower level, and drained the lava to a much lower level, emptying the part of the dyke at A^2, except its congealed walls. Then came closure of the outlet on

the cone, followed by a gradual rise of the lava in the chimney, the frothy surface which almost refilled A² with scoriaceous material.

In dyke (B) that was in the north-west wall of the crater, and may have belonged to the Colle Umberto rift of 1895, we have four falls of level with intermissions; and, no doubt, if these hollow dykes could be approached in a suitable section, other interesting characters would become evident.

I know of one hollow dyke in the Somma cliff that shows a new injection of fluid lava into and through the rubble-filling of an earlier hollow one. Other masses of compact rock are visible that have all the characters of small intrusive sills identical (fig. B, c) with similar ones in the Somma section. Most of the dykes cannot be traced in their complete extension; but others appear as fusiform

Figure B.—HOLLOW AND OTHER DYKES SEEN IN SECTION IN CRATER-WALLS OF VESUVIUS, Nov., 1906.
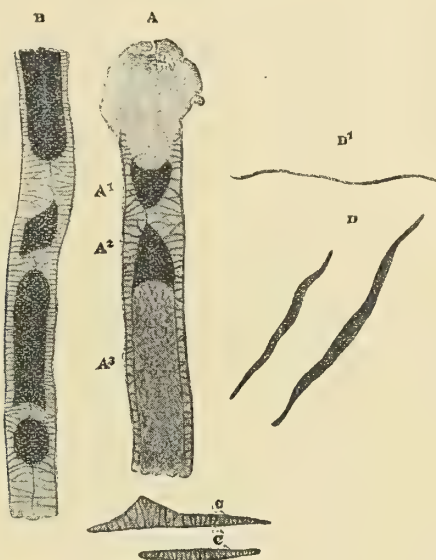
masses in section. Most are vertical, but at (D) two are shown side by side, not far from the present edge of the crater with a marked hade. Their position with reference to the crater-edge is indicated by the irregular line above (D¹).

Passing now to other modifications in the shape of the cone, the point that strikes one is replacement of the relatively sharp angle at its foot, where it joined the Atrio or the Pedimentina by a gentle curve. This is quite apparent in the outline of the mountain in October, 1903, with the photograph taken by the same lens and camera, and from the same spot on the 4th May, 1906 (Pl. III.). We observe how the large amount of material that was ejected and slipped down the slopes as avalanches has collected around the foot of the great cone, filling up the angle.

The average slope of the old cone was 27°, and represented the angle of at least the middle two quarters, the lower and upper quarters being less. Now, the upper half has about that angle, but the lower half has an average of 14°. Near the top, on the south-west side, the angle is as high as 32° or 33°, but this is due to plastering on of sand and dust during the first rains while these materials were still being ejected. The avalanches that swept the side of the cone not only carried down the new ejecta, but peeled and ploughed off a good deal of material that was there previous to the eruption, which is easily capable of verification on the spot. This included most of the railway, which has been completely stripped from the mountain side with the rails, massive sleepers, and concrete bedding (figs. 4 and 5, Pl. VIII.). The same fact is strikingly obvious in comparing the outline of the mountain of 1903 with that of 1907.

Subsidiary Phenomena.

Several observers state that part of the Vesuvian coast was raised, and Prof. Mercalli, aided by Prof. Ambrosini and Dr. Limanowski, collected observations which seem to indicate that an elevation of the coast-line extending from Vico Equense to Portici occurred during the eruptive period, and that the change of level amounted to from 0·30 to 0·40 m. Unfortunately, my recommendation of years ago, subsequently repeated by Prof. Mercalli, that bradysysmic and mareographic observations should be made all over this region, has never been carried out. If this had been done, this elevation of the volcano might have been accurately recorded. This elevatory effect has been observed in at least a dozen paroxysms of Vesuvius, and in that of 1861 was very evident. In fact, it is just possible that such changes of level may precede a great eruption, and in that case would be the much sought-for premonitory warning, and, therefore, of inestimable value.

During the fall of dust and lapilli, the discharges of electricity were, as is usual in such eruptions, very frequent and brilliant, but presented no very striking characters, and seem to have attracted little study. Hardly any damage seems to have been done, for even during the terrible night of April 7–8th, at Ottajano, the telegraphic instruments were able to be worked. At Ottajano railway station the wires were fused at some spots, and the electric-bells were struck.[*]

Around the base of such a volcano as Vesuvius, it not infrequently happens that the erosive and transporting power of rain is more to be feared than damage by falling ejecta. In my paper on the geology of MonteSomma and Vesuvius,[†] I treated rather fully the question of erosive action on volcanoes, as illustrated by Vesuvius, and detailed reference is there made to the destructive effects of heavy

[*] Sabatini, "L' Eruzione Vesuviana dell' Aprile, 1906," p. 22. Roma, 1907.
[†] "The Geology of Monte Somma and Vesuvius."—Quart. Journ. Geol. Soc., vol. xl., 1884.

rains in the intervals of large eruptions. The vast thickness of volcanic alluvial breccias that extend outwards from the base of the mountain was shown to be due to the erosion of the upper, and especially middle, parts of the slope. At that time I attributed all these breccias to an alluvial origin, and, no doubt, the largest proportion is due to that cause. The recent experiences of the eruption of Vesuvius have demonstrated that vast piles of volcanic rubble, or breccias, may be collected at the foot of the cone by the dry slips of fragmentary matter deposited on the upper slopes of the volcano, provided the angle is sufficiently high to allow of this movement of descent. No doubt, were we able to dissect the base of the old cone of Somma, when it attained 2300 metres or 7546 feet in height, we should encounter great deposits of such breccias, now, of course, buried under more recent deposits. That magnificent pile of breccias (Phase III., period 4), 55 metres thick, displayed in the Vallone Grande, may well owe their existence to this cause.* One other explanation has offered itself to my mind, namely, that it is the result of an outburst on the west slopes of the great Somma cone, possibly represented by the Fossa Faraone and the Fossa Vetrana. To that possible conclusion I was led by the extraordinary accumulation at one part only of the surface of the cone. But this may well be a localization of accessory ejecta to a N. W. sector of the cone, such as occurred in the direction of Ottajano in 1906.

This breccia resembles far more that collected around the foot of the great Vesuvian cone during the late eruption than the thick deposits around the foot of Somma, which usually show sorting and false bedding, characteristic of alluvial sorting. I have often, during big rain-storms, made a tour of the *Lagnos* on the north toe of Somma, and watched the great mud-streams pouring down along their bottoms, the finer and lighter scoriaceous or pumice materials, pushing along the heavier blocks, until by the diminishing declivity the water disappeared, in great part by sinkage, leaving the rock-burden as a future addition to the alluvial tuff. Hardly a year passes without some of the towns around the volcano having their streets covered by quite thick deposits brought down by the floods of rain. The whole question hangs on the ratio between the rainfall and the permeability of the surface. The moment the former exceeds the latter, a stream starts, and, from the high angle of its bed, and the incoherence of its bed-materials, soon removes and carries these on downwards to lower levels.

Though the north-east sector of Vesuvius and Somma suffered terribly from the showers of lapilli, little dust fell; and the rain will have to be very great to do much damage, as it will easily disappear by sinkage. That part of the

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* H. J. J.-L., *op. cit.*, Quart. Journ. Geol. Soc., 1884.

volcano to the west of the north and south axis was more or less thickly coated with the fine red and grey dusts which are very slowly permeable, and when washed into the pores of permeable materials, make the latter equally resistant to the penetration of water. On the upper slopes of Somma, at the end of April and beginning of May, the greatest care was required, after rains, to walk anywhere but on the crest, for the moment the feet touched the slope, the wet dust became like the softest clay, or " slip." Once started, one would have slid down hundreds of feet and been overwhelmed by a perfect mud-avalanche or stream.

We should expect that, in all the region where, as we have said, this dust-covering existed, disaster would result from the heavy rains. Such was, in fact, the case. Cercola, S. Sebastiano, Barra, Portici, Resina, Torre del Greco have been from time to time overwhelmed with great mud-flows, or *lava d'acqua*, as the people of the district call them, burying the streets and invading the houses, leaving in a few hours a metre or more of mud.

To prevent this, since the eruption occurred, a sum of about four millions of francs has been spent in constructing walls or dams across any depression that during storms may form a water-course of any importance. These uncemented walls or *briglie* are built of loose blocks of lava and scoria, and have the faces whitewashed, so that they are visible as horizontal streaks of white scattered over the western slopes of the mountain.

Much valuable agricultural land has been destroyed where covered by the new lava-streams, which, from their very rough and rugged surface, will remain for centuries before they will again become fertile, unless some new eruption covers them with fragmentary materials.

In the area where the fall of lapilli was thick, a vast amount of damage was done to the towns at the foot of Monte Somma. Most of the houses in Ottajano and San Giuseppe were wrecked by the enormous weight of material that collected on the flat (*lastrico*) or low-pitched roofs. The walls remained intact, except where levered over by the bending down of the beams of the roofs and floors inserted in them. It was to this collapse of roofs and floors that most of the loss of life was due, as a number of people had collected in the churches to pray under the weak and ill-constructed roofs, instead of getting on to them to clean them. Even during the heaviest part of the fall persons could move about if they covered their heads and shoulders with pillows, tables, and other such improvised shields. Taking the average depth of the deposit to be 0·76 m., as on the Piazza San Francesco, I have, by weighing a cubic metre of the loose ejecta, found that it amounted to about 2000 kilogr. per square metre—that is, over a ton and a half—a weight few roofs could stand.

The south-east sector of the volcano received so little dust that the damage to

the crops was infinitesimal; but all the rest of the mountain slopes, and far away on the Campanian plain in a north-east direction all the crops of annuals and herbaceous plants, were destroyed. The vines, fruit, and other trees and bushes were practically uninjured, except in the lapilli-strewed region, where the stems that were not approaching the vertical were bruised, and on the upper part of the mountain almost stripped by the attrition of the falling stones. That even the *essential ejecta* had lost most of their heat when they reached the ground even as near as the crest of Somma, was shown by the absence of any roasting or carbonizing of the plants buried in them. I dug out at the Canale di Arena the stems of herbaceous weeds, broken and reduced to shreds, but showing no effect of great heat. Even at Ottajano, early in May, the vines were sprouting, and farmers were planting cabbages and lettuces in the newly ejected dust after its first washing by the heavy rains at the end of April that removed part of the saline constituents. In October I was struck on my return to Naples with the little difference in the vegetation from what one would see in any other year at the same season.

Even if a considerable area has been ruined for agriculture by the new lava, I think I can safely say that a larger area has been converted from ragged old lava-streams into cultivable land. Since 1822 most of the eruptions of Vesuvius have consisted principally of the outpouring of lavas, which have covered large areas of the mountain slopes with a surface unsuitable to the growth of crops. The last eruption has spread such a thick mantle of lapilli and dust over the ragged lava-surfaces that in a few years they will be thickly clothed with vegetation. That awful field of wild desolation, the Atrio del Cavallo, and the Val d' Inferno, that was almost impenetrable even to man, could a few months after the eruption be ridden, or even driven, over in all directions.

MINERALOGY OF THE ERUPTION.

The different mineral species that a collector would appropriate when visiting Vesuvius after the late eruption may be easily classified into two definite groups. In the first we should place all those species that were generated during the eruption, or subsequent to it, and as the result of it. This section might be again subdivided into those formed in the lava and scoria, and those deposited either in fissures of the lava or in the fumaroles of the cone and its neighbourhood. In the second section are all those products that enter into the composition of the *accessory or accidental* ejecta. Of these latter very little will be said, because they do not show anything that is not common to other eruptions, and their presence amongst the ejecta is quite a fortuitous one. Prof. Lacroix has paid special attention to them from a purely mineralogical aspect,* extending our knowledge of that

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* "Etude Minéralogique des produits silicatés de l'Eruption du Vésuve (Avril 1906)," &c.—Nouv. Archives du Museum, 4 sér., tome ix. 1907.

portion of the ejected blocks that Archangelo Scacchi extensively studied after the eruption of 1872.

I shall only refer to them in a purely geological or vulcanological point of view —that is, in so far as they are documents bearing evidence for the elucidation of the phenomena of the last convulsion of Vesuvius.

The minerals forming the principal constituents of the *essential ejecta,* namely, the lavas and scoriæ, have already been described, and show nothing of special interest with regard to this eruption. In three of my former papers* I have classified the different ejecta of Vesuvius, and explained their origin and distribution; and I must refer the reader to those papers for fuller details.

In the great throes of the Somma volcano, gigantic craters were produced by the explosive eruptions, the apices of which craters were excavated down into the sub-volcanic platform. The sedimentary rocks and the metamorphic derivatives of these were ejected and spread around the mountain. The great craters were filled in with the ruins of the crater-edges and new volcanic ejecta; so that could we make a complete dissection of the mountain, it would appear in shape like a huge hob-nail. Paroxysmal eruptions that have occurred later than the explosive ones cannot reach the sub-volcanic platform, but can extend only more or less into the plug or neck that fills the largest crater of the explosive period. It is obvious, therefore, that such a paroxysm will only eject *those materials that have been deposited there since the last explosive outburst.* Such materials will consist of lava-flows, dykes, scoriæ, lapilli, dust, and any sedimentary or metamorphic blocks that have fallen back from the crumbling edges of the crater where they had been deposited as earlier ejecta.

It is obvious, therefore, that it is only fragments of these materials that we expect to encounter in the ejecta of such a paroxysm as that of April, 1906; and, in fact, that is just what we do, and they may be conveniently classified as follows:—

1. *Ancient lava and dyke rock* :—

    (*a*) Fresh and unaltered.

    (*b*) Rocks such as (*a*) metamorphosed by prolonged heat under pressure near the volcanic chimney with infilling of cavities by sublimed silicates and other minerals, and by residual juice from the fluid lava of the chimney.

    (*c*) Ancient fumarolized rocks such as (*a*) that have been subject to metamorphism as in (*b*).

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* "Geology of Monte Somma and Vesuvius "—Quart. Journ. Geol. Soc., vol. xl., p. 35, 1884 ; "On the Fragmentary Ejecta of Volcanoes "—Proc. Geol. Assoc., vol. ix., 1886 ; and " Ejected Blocks of Monte Somma, Part I."—Trans. Edinburgh Geol. Soc., vol. vi., 1893.

2. *Ancient scoriæ, lapilli, and dust* :—

    (*d*) Fresh and unaltered.

    (*e*) Same changes as in (*b*).

    (*f*) Same changes as in (*c*).

3. *Ancient ejected blocks of sedimentary origin, and their metamorphic derivatives* that have again been ejected and again buried, and have been subjected to the same treatment as (*a*) and (*b*).

Whether we examine the gigantic blocks scattered by the late outburst over the slopes of the cone, around its foot, or the small lapilli that buried Ottajano, we find they have the same characters. The principal ones are composed of fragments of dyke-rocks or lavas. Many are as fresh when broken as the day they originally cooled; some have undergone partial fusion; and others again have had their open fissures or cavities filled by a black glass. Such blocks were fairly frequent in the last eruption. Sometimes this black glass entirely fills the cavity, sometimes only in part, being insufficient in quantity to do so, or being blown up by bubbles.* I have in my collection a specimen of an old cavernous lava, in which the black glass hangs from what was the roof as a great thick blob or stalactite, showing its great viscosity at the moment it reached that situation. I have arranged in the following Table the analyses published by Signor Matteucci.†

* In one specimen I collected of this eruption a cavity is lined, or coated, with this black glass, from which some remarkably limpid and well-terminated leucites have separated.

† *Op. cit.*, p. 851.

[TABLE.

EJECTED BLOCKS OF OLD LAVA OR DYKE-ROCK CONTAINING PATCHES OF BLACK GLASS.

	Leucitite Matrix. Matteucci.	Leucittephrite Matrix. Lacroix.	Compact Vitreous Portion. Matteucci.	Vitreous Portion. Lacroix.
SiO_2 . . .	47·451	48·20	51·808	53·10
FeO . . .	4·554	4·30	7·197	4·77
Fe_2O_3 . . .	5·323	3·29	—	0·07
Al_2O_3 . . .	17·340*	18·12	20·159	20·70
CaO . . .	9·438	8·40	2·941	3·18
MgO . . .	4·976	4·64	0·596	1·77
K_2O . . .	7·739	8·99	5·709	5·84
Na_2O . . .	2·355	2·51	11·212	9·10
H_2O . . .	—	—	—	0·70
TiO_2 . . .	—	1·59	—	0·47
P_2O_5 . . .	—	0·38	—	—
	99·176	100·42	99·622	99·70

From these it will be seen that the amount of silica and soda is greater than in the matrix rock and in recent lavas. The question arises therefore as to the origin of this tachylitic glass that fills these cavities. I quite agree with M. Lacroix, that it is not due (in most cases, at least) to partial refusion of the matrix.† It may be a residual glassy juice, derived from the fluid magma that must have existed in the precincts of this cavernous matrix when that was penetrated by this glass. It is more likely, I think, to be due to two other possible causes. The first is the fusion of silicate and other minerals that sublimed and were deposited in these fissures and cavities, and later by a rise of temperature and the presence of alkaline chlorides or sulphates as fluxes were re-fused.‡ I have, in fact, frequently met with such partial fusion of minerals in geodes in ejected blocks of this region. In other cases such tachylytic glass may be due to the fluxion of sublimed alkaline chlorides with some of the leucitic material. This matrix-rock is quite similar to those that are frequently crowded with zeolitic deposits, the re-fusion of which with a certain amount of the minerals forming the wall of the cavity may easily furnish a glass of this composition. In fact, some of the figures given by M. Lacroix§ show partial fusion of the rock-forming minerals

* Also with P_2O_5.   † *Op. cit.*, p. 45.

‡ Since writing the above some of these specimens are thickly crusted with alkaline chlorides which have effloresced from the pores of the rock.   § *Op. cit.*, pl. III.

and some efforts at repair as the rock cooled. Other rocks such as these also contain nepheline, augite, amphibole in very varying proportions, that could undergo fusion when exposed to suitable conditions, especially with alkaline chlorides or sulphates as fluxes. It is obvious, therefore, that such a black glass would have no very definite composition; but in either case we should be prepared to find an increase in the alkalies such as the analyses show. The other marked feature in the composition of this glass is the diminution of lime and magnesia, for which several hypotheses might be offered.

Lacroix* does not admit this black glass to be a result of partial re-fusion of the rock, since, he thinks, it would not recrystallize with much larger and finer crystalline contents, and also that it would be a more basic material in composition. The facts and the remarks I have above made about them will, I think, quite remove those difficulties. Besides, I have often collected blocks of semi-fused old lavas having the same characters as the above-mentioned ones, and that were ejected and fell at my feet, with Vesuvius in its chronic lava-cake, cone-forming stage. Specimens of these in my museum are a nuisance on account of the constant efflorescence of chlorides from their surface, and such efflorescence occurs from the cracks of this black glass under discussion. Even in the tachylytic glasses there is a marked difference in composition, especially in the iron. Magnesia and soda also vary considerably.

Rather frequent in ejecta of this eruption were large or small masses of a spongy, vesicular glass—a cooled, glassy froth, in fact, either filling clefts and cavities in old blocks of lava, but more frequently enveloped in a crust of new compact lava, so constituting a volcanic dumpling. Sig. Matteucci also records their presence. I have collected similar material in the contents of dumplings of 1872 and other eruptions. Sig. Matteucci gives an analysis, showing this substance to be largely a lime and alumina silicate.†

BLOCK OF LEUCITITE WITH VITREOUS SEPARATION AND OF LIME SILICATE.

	Crystalline Part.	"Pumiceous" Vitreous Part.
SiO_2 . . .	48·372	58·508
FeO . . .	4·904	5·300
Fe_2O_3 . . .	4·500	3·556
Al_2O_3 (with P_2O_5) .	16·372	10·313
CaO . . .	11·611	12·648
MgO . . .	6·916	1·506
K_2O . . .	5·147	3·398
Na_2O . . .	1·448	3·900

These masses I met with of all sizes, ranging from that of a nut up to a bomb-like block 0·60 m. in diameter. They were usually coated with a black crust of

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Op. cit., p. 42,   † *Op. cit,*

cooled magma. The vesicles are sometimes so small as to give the mass the appearance of a fine sandstone, and in others reaching a size in which the fist can be placed. Under the microscope several mineral species have been described —quartz, diopside, wollastonite, by M. Lacroix; and in some I found felspars. I consider these masses to be similar to the black-glass fillings above described, but which in this case had contained H_2O, and had vesiculized by expansion as pressure was relieved.

The next class either consists of pieces of old lavas, fissured or cavernous, or is more frequently composed of fragments of lavas, scoriæ, and lapilli adhering together. The cavities or interspaces of these imperfectly agglomerated masses are lined by a series of interesting minerals that have been deposited therein at a later date to the emplacement of these fragmentary materials near the volcanic chimney, from which position they were eventually torn and ejected in this eruption.

Some of these specimens are rather striking, as their interspaces are crowded with long, slender, black, needle-like prisms of amphibole. Others glisten with numerous glassy or white crystals covering all free surfaces. The minerals so occurring have been elaborately studied by M. Lacroix* and Sig. Zambinelli† from the mineralogist's point of view. I give here a list of the minerals so far recorded :—

Orthoclase.	Davyne.	Magnetite.
Acid Oligoclase.+	Microsommite.	Hæmatite.
Anorthite.+	Hornblende.	Fluorite.
Leucite.	Augite.	Apatite.
Sodalite.	Ægirine.	Anhydrite.
Cavolinite.	Garnet.+	Sphene.+
Nepheline.	Biotite.	

Those minerals without a cross I have observed myself, and those so marked have been detected either by M. Lacroix‡ or by Sig. Zambinelli, and I shall not therefore further refer to them in detail. Suffice it to say that they show a striking resemblance to those produced under similar conditions in 1872, and so carefully studied by A. Scacchi.

The order of their deposition in most cases seems to have been—orthoclase and other felspars; then the augites and hornblendes; next the felspathoids. The

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* *Op. cit.*

† "Notizie mineralogiche sull' eruzione Vesuviana dell' Aprile, 1906."—Atti d. R. Accad. d. Sc. fis. e mat. di Napoli, vol. xiii., serie 2ª. Novembre, 1906.

‡ *Op. cit.*

magnetite seems to have proceeded right through the process, and the other groups of minerals overlap.

The method of their deposition is what earlier authors referred to as *sublimates.* Of course a true sublimate is a material that has been heated until it reaches the gaseous state, and that again condenses into the solid form on any surface sufficiently cold to reduce the temperature of such gas or vapour to that at which the crystals of the substance can form. It is unquestionably certain that where such a temperature was reached, the same mineral species that have acted as condensers would at least have been fused. Perhaps the *tachylyte* infillings may, in fact, represent such a condition. But sublimation has been used by many writers in the sense of one vapour acting as a vehicle for others, and depositing by a slight reduction of temperature part of its burden as crystals. M. Lacroix affirms that these minerals were deposited by *autopneumatolysis.* This is a new word used of late years for an old and well-understood phenomenon. In the present instance these minerals were deposited by a deep fumarolic or emanational process, and the minerals we see are the result of the *fractional condensation* of the mixed vapour at that particular spot. We could admit the word *pneumatolysis,* but *autopneumatolysis* applies to the deposition of crystals in cavities, fissures, and vesicles of the magma from which the substances emanate, and not from extraneous sources.

In the present instance, such is not the case, for the mineral-forming vapour came from a greater or less distance, and, in fact, we have to deal with a contact metamorphism. There has been little dialysis or osmotic interchange, as the *active* magma has approximately the same composition as the passive surrounding solid matrix. Even where, as we shall see later, the original minerals of the matrix have been changed, the mass analysis would prove to be much the same. In fact, dialysis *seems to take place in the process of metamorphism mainly through fluid and solid media molecularly contiguous, in which the solid may be considered as a fluid with very high viscosity.* The open brecciated character of the richest sublimate-charged ejecta shows the absence of such continuity. All that has taken place is a simple re-arrangement of the molecules to form new minerals or varieties of those already existing.

No doubt a few additions have been made, as we shall see in discussing these changes; but such contributions are of the character of gifts rather than of exchanges. In fact, we have the first and most feeble grade of that process which I have described as the *dialytic* or *osmotic theory of metamorphism.*

I laid down in considerable detail the general principles of the conditions under which certain rock-forming minerals came into existence in the magmas, in a paper I published over twenty years ago.* I there showed that leucite and

* " The Relationship of the Structure of Rocks to the Conditions of their Formation."—Scient. Proc. Roy. Dublin Soc., vol. v., 1886.

augite were minerals, when intratelluric in origin, which were produced at no great depth; whereas their competitors for the same chemical constituents, as potash, hornblende, orthoclase, and mica, could only come into existence *in a magma* under abyssal conditions.

Now, although such minerals as specially hornblende, orthoclase, and biotite usually require abyssal conditions *when crystallizing out from solution in other fused silicates*, as in a paste or magma, they can be formed at a temperature of an ordinary kitchen oven, when they are deposited by " *sublimation* " or *pneumatolysis*. In another paper of mine* I drew attention to very extensive deposition of large crystals of biotite and hornblende, on a quaternary fossil bone that still retained a large part (five-and-a-half per cent.) of its organic matter. When this bone, covered with these silicates, usually abyssal in origin, was heated, it blackened and gave off the odour characteristic of roasted or burnt bone. Now, at Faiano, in the "pipernoïd tuff" from which these bones were removed, the commonest of the above-mentioned silicates are augites, nepheline, and fluorite—in fact, the same companions as we have in these drusy blocks of the late eruption of Vesuvius. These facts, I think, go to prove that the mineral-lined blocks ejected from Vesuvius owe their enclosed minerals to probably volatile fluorides, chlorides, &c., as the vehicle that carried them from the magma and deposited them in the rock in which we now find them.

These old lavas, scoriæ, breccias, &c., containing these new minerals in their cavities, have, as has already been touched upon, undergone a certain amount of metamorphism, or alteration. Lacroix† has described in great detail these changes, which have been recorded by several observers, and which I have verified by slices I have cut and have examined. The most interesting are the loosely agglomerated masses of old fragmentary materials of the cone which are only just soldered together at their points of contact, leaving many spaces in which the neogenic minerals have been deposited. We find that on cutting sections of the old angular fragments, the constituent minerals of the rock have been altered and modified to a greater or less distance from the surface. The chief changes are the bleaching of the augites and the gradual conversion of them to ægirine, whilst the leucite is partly converted into a microsommite and sometimes into orthoclase.

It is obvious that if these breccias remained as a relatively incoherent mass, the molecular contiguity between the active magma and passive matrix could practically only be through gases; in other words, transmission could not be through the solid, but only through the gasiform infillings of the intervening spaces.

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* " On the Formation at Low Temperatures of certain Fluorides, Silicates, Oxides, &c."—Geol. Mag. Dec. IV., vol. ii., p. 309.   July, 1895.

† *Op. cit.*

I avoid laying any stress upon the differences of the amphiboles (hornblende) and nephelines, for mineralogists have not yet settled upon the characters that define the many different species of these mineral families.

One of the drusic minerals is leucite. Whether this required a higher temperature, the absence of fluorides, chlorides, or sulphates in the vapour from which it was deposited is an interesting problem. That it is not an abyssal mineral I demonstrated many years ago, and M. Lacroix has re-discovered this fact.* Accidental minerals enclosed in the few pieces of pumices, pumiceous scoriæ, and scoriæ examined by him are referred to as essential constituents. The future student of Vesuvius will be met by a vast amount of casual uncorrelated notes on different ejecta, made all the more complicated by a profuse and unnecessary nomenclature.

The third class of ejecta may be classed as fumarolized rocks, in which true surface fumarolic minerals have been deposited, and in which the volcanic vapours have acted in a more or less destructive manner on the rock constituents. These blocks and their contents obviously come from no great depth, and are quite similar to those so frequently met with quite at the surface. In some blocks we have to deal with agglomerates and breccias, and in other larger pieces of older lavas and dyke rock.

Furthermore, we can separate them into those only slightly altered and reddened, and those highly fumarolized and converted into red, orange, or light yellow masses. It was in two blocks of slightly altered, reddened scoria that the cavities were found lined with halite and sylvite in beautiful cubes up to a centimetre or more in diameter. Associated with this was a new mineral, which I have described,† and which has subsequently been studied crystallographically by Mr. L. J. Spencer. This mineral, which I have called chlormanganokalite, is a double chloride of potash and manganese, as results from the following analysis made in May, 1907, on nearly a gram of material, which gave the following results :—

K	.	.	.	36·34	or	KCl	.	.	.	69·42
Mn	.	.	.	11·52		$MnCl_2$.	.	.	.	26·45
Cl	.	.	.	48·13		$MgCl_2$.	.	.	.	0·16
Mg	.	.	.	0·04		Na_2SO_4 .	.	.	.	1·19
Na	.	.	.	0·38		H_2O .	.	.	.	1·52
SO_4	.	.	.	0·81		Insoluble	.	.	.	0·71
H_2O	.	.	.	1·52						———
Insoluble	.	.	.	0·71						99·45

99·45

* I cannot help thinking that M. Lacroix has not given sufficient attention to the literature of Vesuvian eruptions, including papers by Prof. Scacchi and myself; nor are his specimens always adequately localized or their field relations recorded.

† *Nature*, May 31st, 1906, vol. lxxiv., pp. 103, 104; and Johnston-Lavis and L. J. Spencer, "On

The chlormanganokalite is in beautiful crystals, some attaining 5 mm. to 1 cm. in diameter, and are superposed on the halite and sylvite. In another block, in which fumarolization had converted the whole mass into a lemon-yellow mass, chlormanganokalite crystals are over a centimetre in diameter, but are damaged by a coating of some iron-chlorides. Here again this mineral is associated with crystals of the alkaline chlorides, and with a rare form of hematite, in brilliant spear-like-looking crystals, which Mr. J. L. Spencer, who has measured them,[*] finds to be acute scalenohedra, exhibiting the following faces:—$\{31\bar{3}\} = \{24\bar{6}1\}$, or the form β of text-books.

This hematite afforded me the following composition :—

Insol. in nitro-hydrochloric acid, .	4·784 (attached silicates).	
Fe_2O_3, ...	94·791	
S, ...	0·432	Probably adherent
As, ...	traces	sulphur of realgar.

This form of hematite is quite new to me at Vesuvius, neither do I know of its ever being detected before. Such forms of hematite are, so far, known as occurring at an " island in the Red Sea." The crystals are distinctly magnetic. Zambinelli[†] very fully described the minerals that have formed by sublimation on the lava-flows.

Sal Ammoniac was abundant, as crusts, around fumaroles scattered over the lava-streams, where these had flowed over ground containing organic matter, confirming the old theory that this mineral is derived from the decomposition of such matter, and its ammonia being converted into a chloride by the hydrochloric acid escaping from the lava.[‡] Halite and sylvite, in varying proportions, were likewise deposited around fumaroles and cracks, and in some places were associated with iron-chloride and various other chlorides. These were still being deposited on the lava at Boscotrecase in November, 1906.

Hœmatite in the usual scales, and small crystals, were to be met in the scoria near the fumaroles of the lava. Cotunnite was also said to be found; and though I received specimens as having been so found, I did not see or collect them myself.

Chlormanganokalite, a New Vesuvian Mineral "; with notes on some of the associated minerals. Min. Mag., vol. xv., No. 68, April, 1908.

[*] H. J. J.-L. and L. J. Spencer, Min. Mag., vol. xv., No. 68, pp. 54–61.

[†] *Op. cit.*

[‡] See an interesting crystallographic study by F. Slavick, Bull. Internat. de l'Acad. des Sc. de Bohême, 1907.

Sulphur I saw in minute quantities, just sufficient for recognition. On the N. N. E. side of the cone, the apron of lava, whether it be formed during this eruption or anterior to it, exhibits a large number of fissures, extending from the crater-edge radially down to the level of the top of the Colle Margherita.

These fissures gave forth considerable quantities of vapour, constituting quite a large fumarole-field. These fumaroles have remained active for many months after the eruption. In fact, a very large portion of the vapour of the volcano found its escape by these fissures when the main vent had become choked by the falling-in of materials of the eruption. These fissures point to a very weakened condition of the cone in this direction; in fact, in the line of lowest truncation during the great blast, and in the line in which the materials were directed. These fissures are bunged or choked by the large collection of debris at the base of the cone; but in the Atrio, in the same azimuth, a series of fumaroles have shown through the ejecta-mantle, right away to the Somma escarpment. For months after the eruption, these fumaroles afforded abundant deposits of sulphur, sulphides, chlorides, sulphates, and other rare sublimates.

Sulphur occurred in most of the fumaroles, from the crater-edge to the cliff of Somma, and chlorides of iron, with potash and soda, were likewise to be met with in nearly all. Realgar, mostly in globular, fused crusts, mixed with seleno-sulphur, was chiefly deposited on the edges of those fissures on the side of the cone. Hematite, as usual, could be found in many of the more important fumaroles. Galena, a new sublimate at Vesuvius, was discovered associated with pyrite and chalcopyrite. The last-named minerals, also new as sublimates, were found soon after the eruption in these fissures at the crater-edge. Sig. Zambinelli mentions them as being found in the crater; but that is not so, as no human being could enter it in May, when this material was collected. Amongst the fumaroles on the cone-flank, near the crater-edge, were rare specimens of anglesite, pseudocotunnite, and later beautiful small crystals of cotunnite, the finest I ever saw from Vesuvius. Very fine tenorite has been produced at the hotter fumaroles on the slope of the cone. Apthitalite has also been recorded, but in very poor and limited quantities.

An extremely interesting discovery is a new mineral analysed by Prof. A. Casoria.* It is a hydrated silicate of nickel and magnesia, and is, no doubt, a variety of garnierite, quite new to Vesuvius.

It will thus be evident that Vesuvius has not only afforded a series of eruptive phenomena of great interest from a general point of view in the study of volcanoes, but has produced much material for the study of volcanic mineralogy. In fact,

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* " Sopra un nuovo minerale di Nichelio nei prodotti dell' eruzione Vesuviana dell' Aprile, 1906." —Ann. d. R. Scuola Sup. d' Agric. di Portici, vol. vii.

Vesuvius has every reason to maintain its reputation as the most interesting type-volcano of the world, which title I have on several occasions ventured to claim for it. In this study I have endeavoured to limit myself to purely vulcanological issues, and to study only those phenomena that would help us to elucidate the highly complex problems of volcanic action. Minor details of petrography and mineralogy have been purposely eliminated to make the main physical and chemical aspects of the question stand out more clearly.

Trans. R. Dubl. Soc. Ser. II. Vol. IX.

Plate III.

Johnston-Lavis, Phot.

The aspect of the great cone of Vesuvius on May 4 th, 1906 as seen from the Punta del Nasone on M. Somma looking due South. The dotted line is that of the outline of Vesuvus in Oct 1903 taken with the same camera and lens, and represents, except for a faint variation at the extreme summit, the actual outline of the cone before truncated by the late eruption.
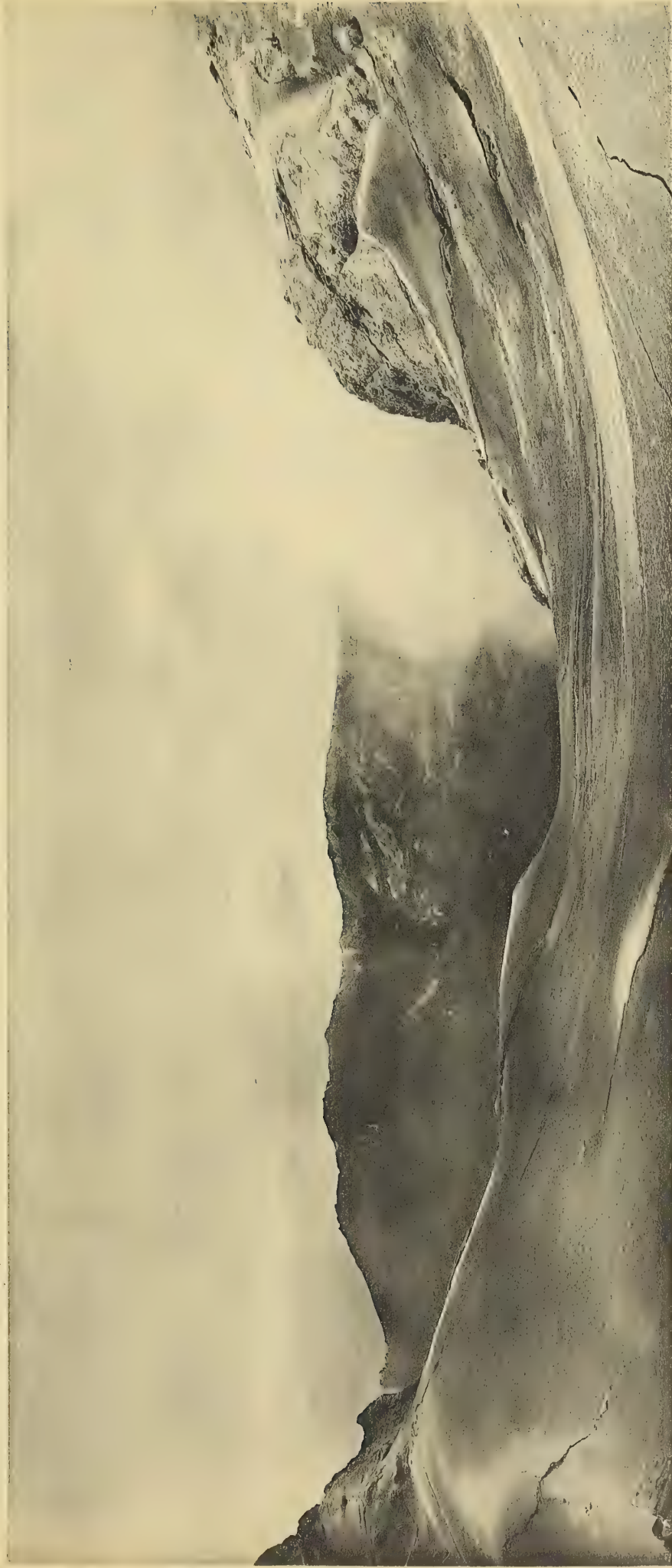
Panorama of the new crater from the N. lip looking due S. on May 2 nd, 1906.
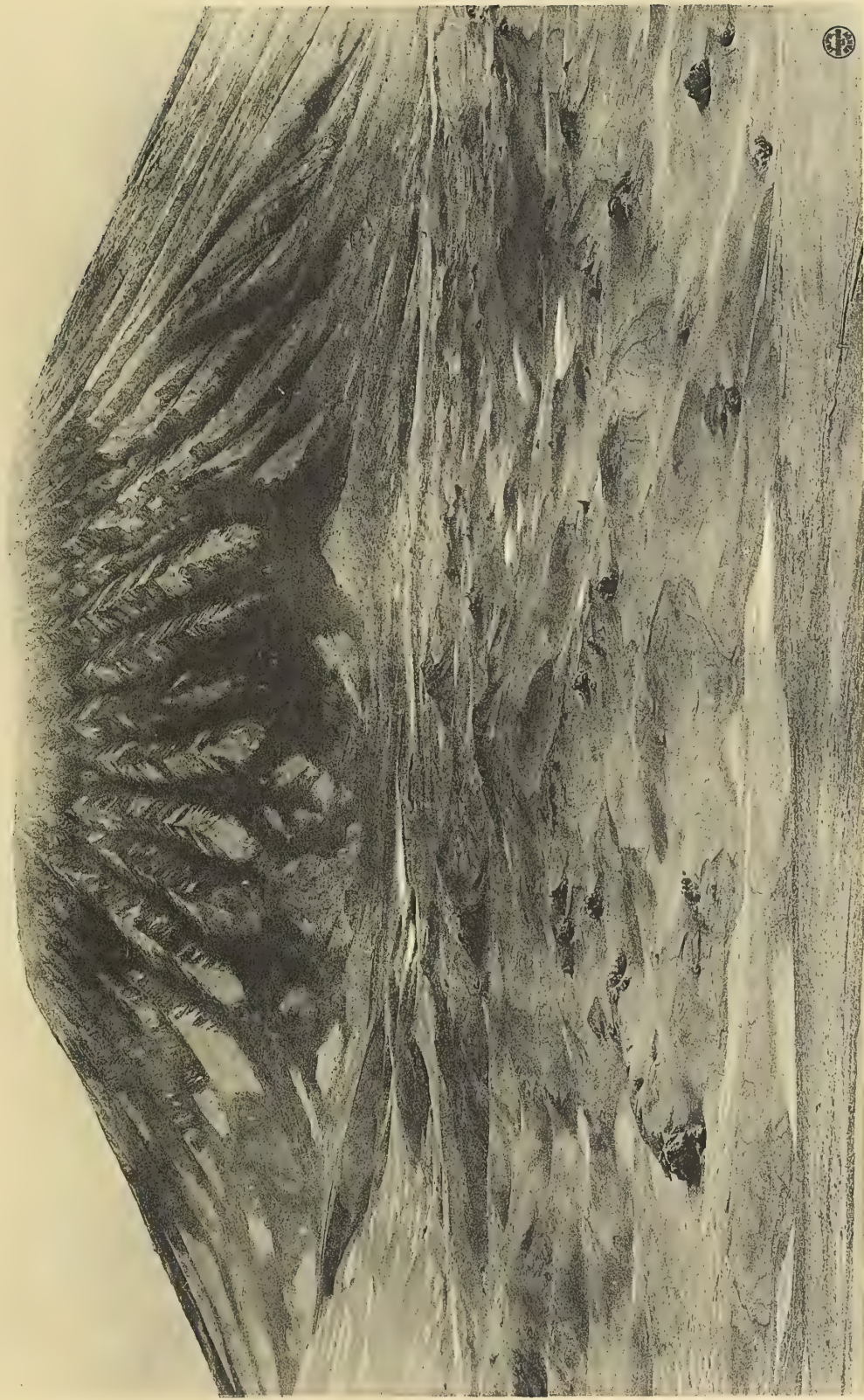
Johnston-Lavis, Phot.

The great cone of Vesuvius as seen from the W. at the foot of the Colle Umberto, looking due E. across the Atrio on May 3rd 1906, to show the truncation of its top and the remarkable barrancos formed on its sides by the slipping of loose fragmentary ejecta.

Johnston-Lavis, Phot.

Lower terminations of the inter-barranco ridges near the Atrio on the N. N. E. slope of the great cone of Vesuvius. Observe the height of the man standing at the foot of the E. wall and compare with height of barranco wall.

Figure 1

Section of the lapilli and dust deposit in a garden in Ottajano. The metre measure rests at its lower end on the old garden soil. All above was ejected between the 7 th and 8 th of April, 1906.
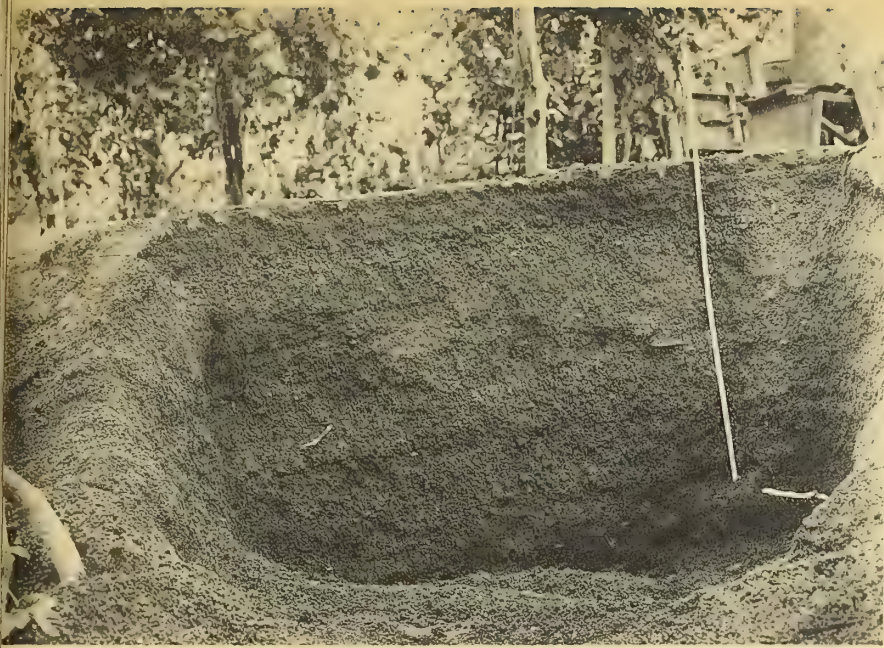
Figure 2

The lapilli deposit near the station of S. Giuseppe. By an accident to the negative a few centimetres at the top are missing. The bottom essential ejecta are well shown.

Figure 3

The great cone from the S. S. W. after the eruption of Ap. 1906 showing a gigantic block that weighed at least 30 tons. Observe the metre measure leaning against the block a little to the right of the centre.

FIGURE 4

The slopes at the foot of the great cone on the W. S. W. side below where the the funicular ry. station, boiler house, restaurant and stables stood. Two of the boilers are seen, one to the left of the middle.

FIGURE 5

Remains of the funicular ry. (to left of centre of picture) The station and restaurant stood below the bank and ravine in the foreground. The ravines were cut out by avalanches of loose materials from the cone. The feeble effect of rains is shown in the wash of materials over the bank of the ravine in the left lower corner. Photo. taken 27 April, 1906.
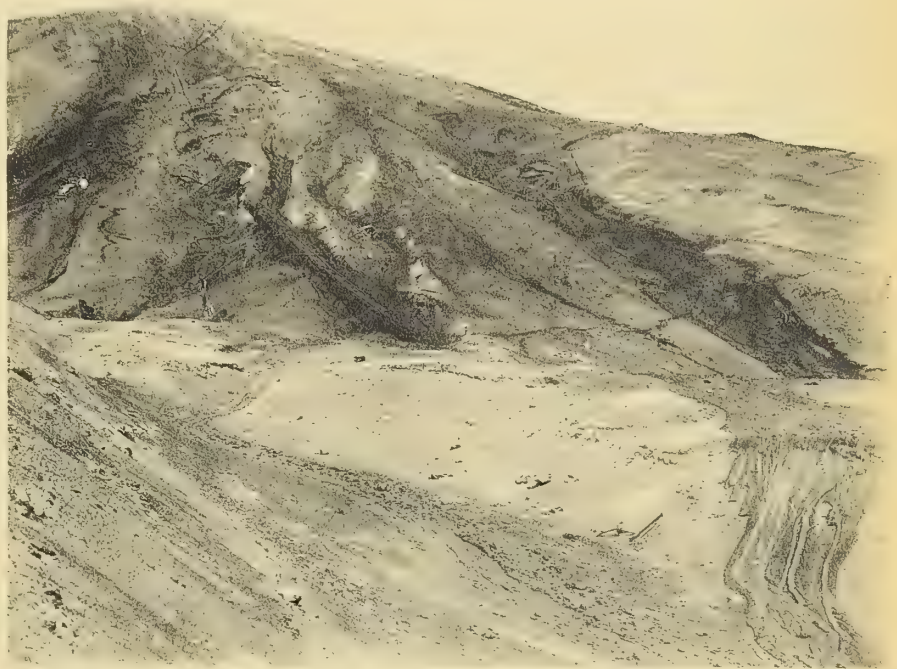
FIGURE 6

The last stage of the eruption as seen from the summit of Somma. The final dust ejections, 4 May 1907.

Figure 7

The large falls of fragmentary ejecta added much to the screes against the escarpment of M. Somma ; their slipping has produced the peculiar fan like streaking seen in this photo. taken the 29 April, 1906.

Figure 8

Lava that poured down the valley above Boscotrecase. Observe the lateral moraines left at the edges of the ravine, the lava smears on its sides, and the scoriaceous covering of the remains of the stream at the bottom.

Figure 9

The same ravine showing the lateral moraine of scoria on its edge in the foreground.

FIGURE 10

Great cone of Vesuvius seen from the south before the eruption. Observe the lava humps of 1885 on left limb of cone and those of 1883 on the right.

FIGURE 11

Lava crossing a road at right angles near Boscotrecase. Observe the gradual pushing over of one of the walls.

FIGURE 12

Lava that had flowed down one of the streets of Boscotrecase. The thickness at a short distance from the front is seen to attain the first floor of the houses. The paving stones over which it flowed were cut from an earlier Vesuvian lava.

FIGURE 13

Lava stream near cemetery of Torre Annunziata of considerable breadth, and deep enough to bury the two storied house one story. It has caused expansion of the rails and made them buckle, as seen at the edge of the stream.

FIGURE 14

Lava that invaded a railway-cutting and flowed along it between Boscotrecase and Torre Annunziata.

FIGURE 15

Bridge over railway cutting above Fig. 14 that gave passage to lava when this was very fluid, but, as the lava became more pasty, it collected behind the arch, piled itself up, and had commenced to push the bridge bodily forward.

FIGURE 16

Lava that invaded the court of the
villa of M. and T. Borosio at Boscotrecase.

FIGURE 17

Four one storied houses buried up to
their vaulted roofs in lava at the Rione
Oratorio, Boscotrecase. To the man's left
seated on the roof is a chimney, and another
cylindrical one broken off lies at the
corner of the houses nearest the observer.

FIGURE 18

A volcanic dumpling or flotation bomb.
The nucleus is of masonry. The thin
compact crust of lava has been partly
broken away to show the nucleus. The
crust is, however, intact at the lower
front part to the left of the figure and at
the top.

Johnston-Lavis, Phot.

New Vesuvian lava below Boscotrecase showing the scoria « *aa* » surface where it invaded and covered highly cultivated gardens and vineyards. The truncation of the cone is well seen from its S. S. E. aspect.

Johnston-Lavis, Phot.

Vesuvius and Somma seen from Terzigno in Nov. 1906, showing their relative position, the truncation of the great cone of Vesuvius, and the covering of lapilli on the upper slopes and ridge of Somma. The observer is looking W.

Plate XVI.

Johnston-Lavis, Phot.

Looking down into the crater of Vesuvius from the S. lip, Nov 2nd 1906. The gap on the opposite edge is the spot from which Pl. IV was taken.

Plate X
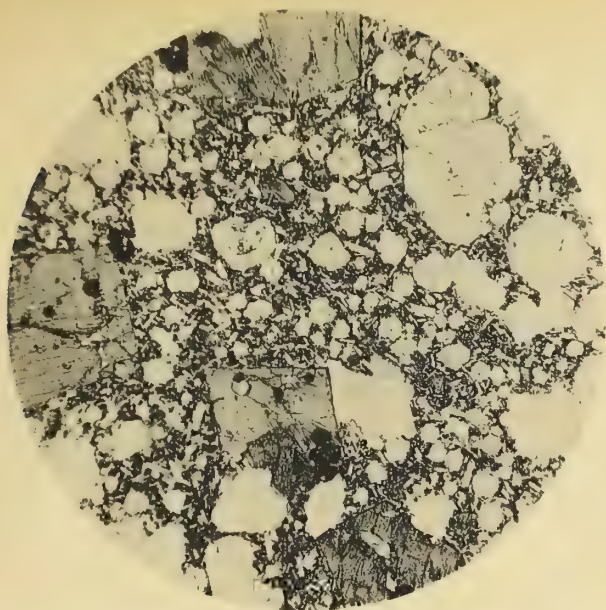
FIGURE 20. — Specimen 3602. Interior of lava 1895-1899, $\times$ 17½ d.
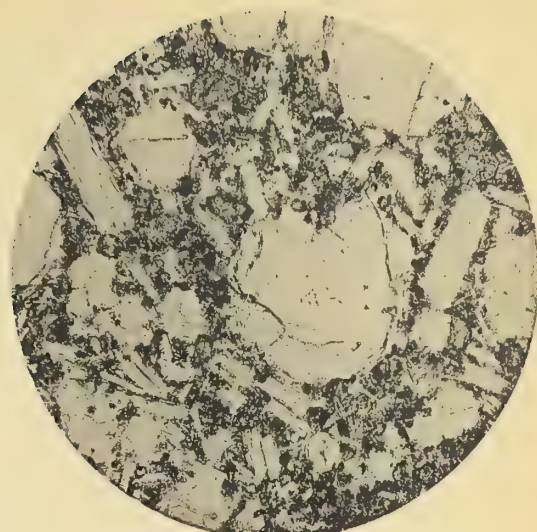
FIGURE 21. — Same as 20 but $\times$ 80 d.
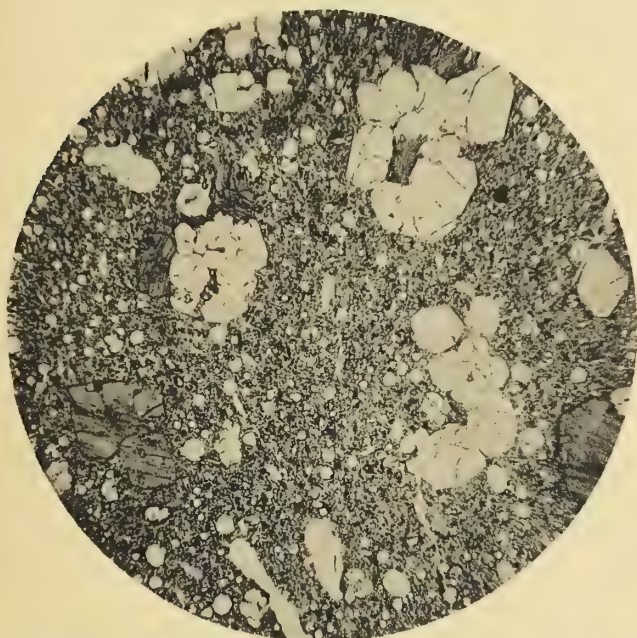
FIGURE 22. — Specimen 3604, lava Ap. 1906 that flowed into a cistern at Bosco $\times$ 17½ d.
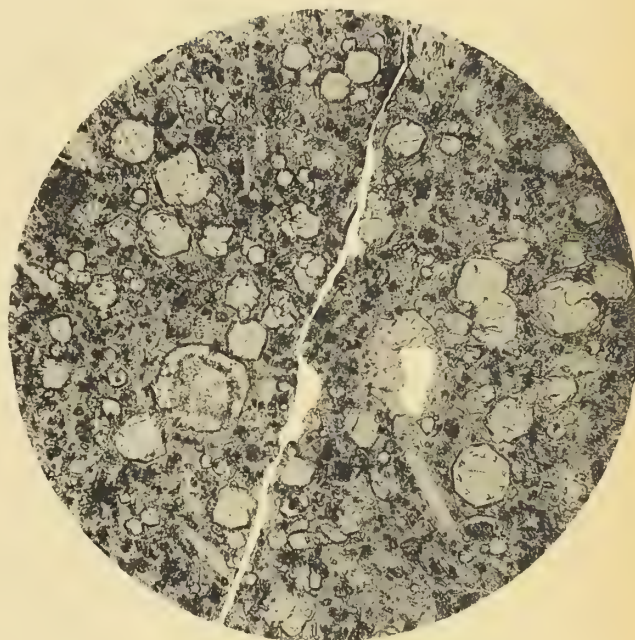
FIGURE 23. — Same as 22 $\times$ 80 d.
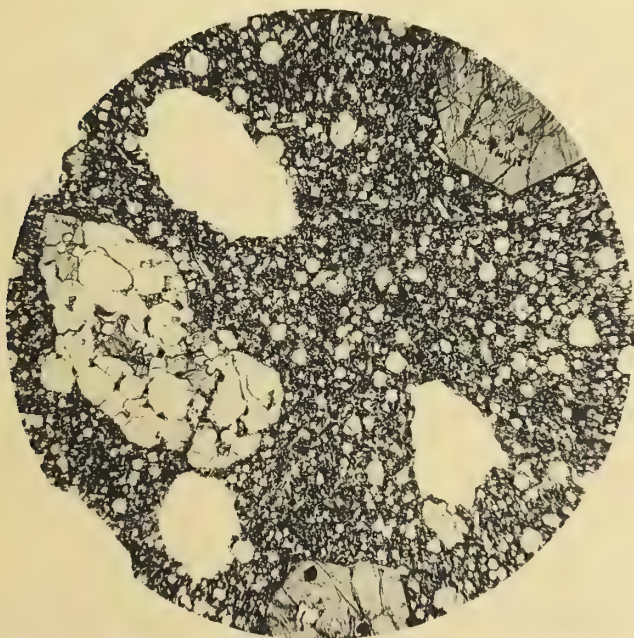
FIGURE 24. — Specimen X, interior of lava stream Ap. 1906, $\times$ 17½ d.

n-Lavis, Phot.
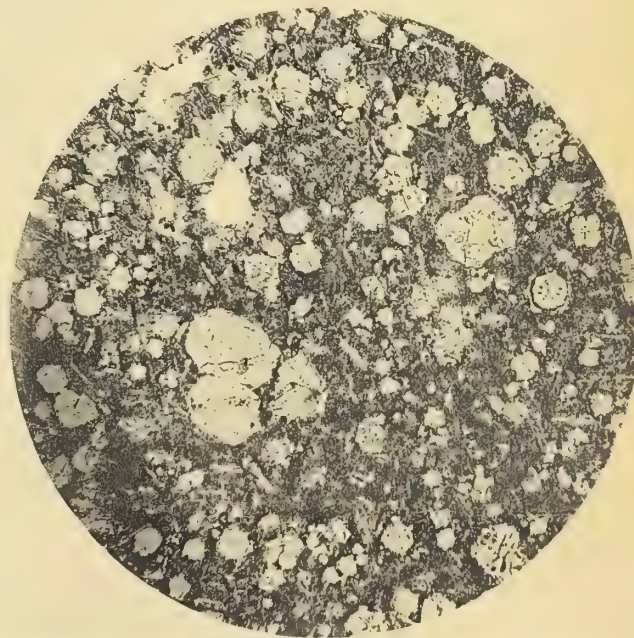
FIGURE 25. — Specimen 3610. Interior of 2nd lava stream near. Casa Fiorenza, Ap. 1906. $\times$ 80 d.

Plate XVII
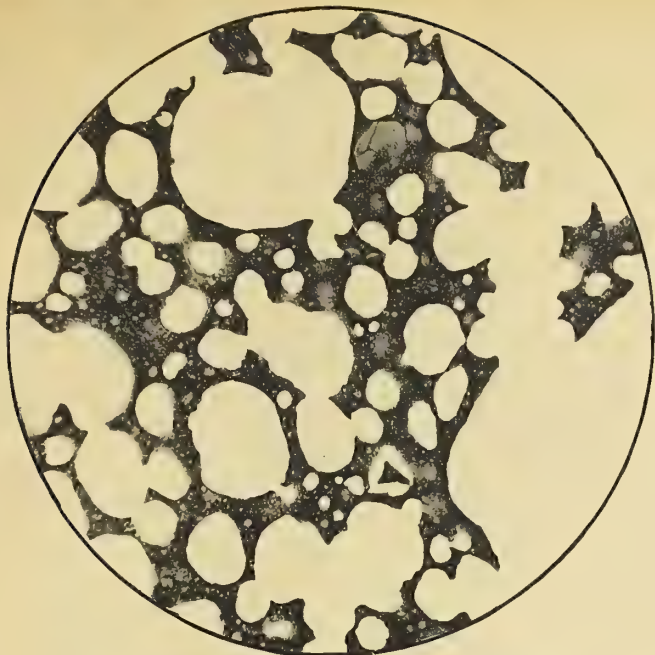
FIGURE 33. — Spec. 3369. Lower Essential Scoria (5 cm) (**a**)
Erupt. Ap. 1906. Ottajano   ×17½ d.

FIGURE 34. — Spec. 3369 same (**a**)   ×80 d.
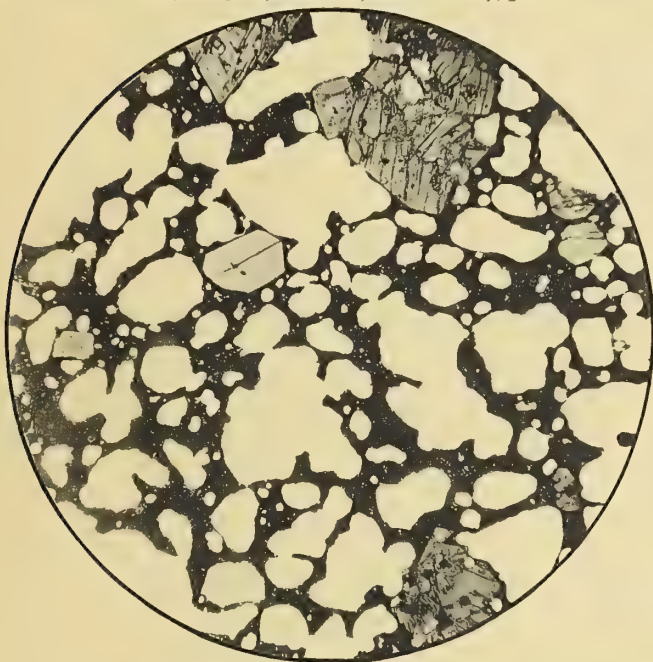
FIGURE 35. — Spec. 3670. 2nd Essential Scoria (15 cm) (**b**)
Erupt. Ap. 1906. Ottajano.   ×17½ d.
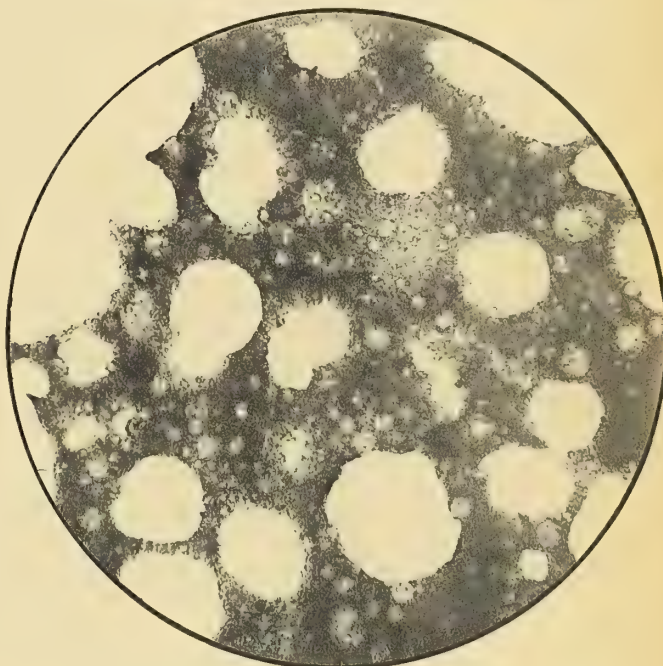
FIGURE 36. — Spec. 3670. Same (**b**)   ×80 d.
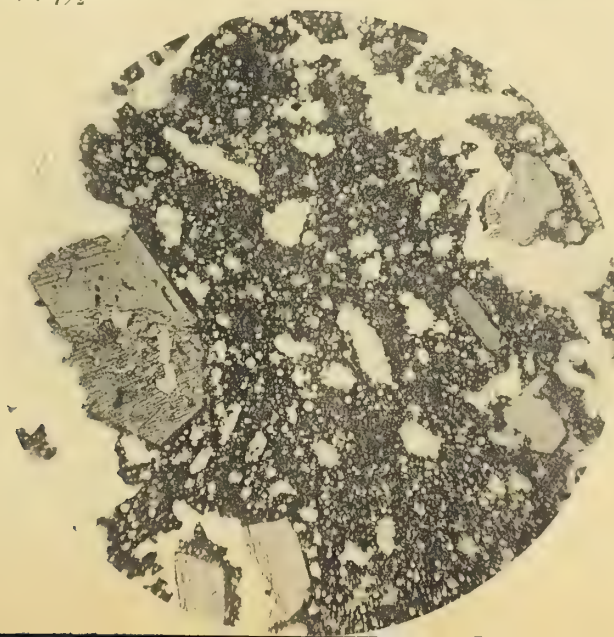
FIGURE 37
Spec. 3657. Essential Scoria (**c**)
late in erupt. of Ap. 1906. Slopes of G.
×17½ d.

PLATE XIX.

J. A. Perret, phot.

Dry avalanche on W. side of Vesuvius towards the end of the eruption of April, 1906.

Trans. R. Dublin Soc. Ser. II, Vol. IX.

Plate XX

Sections near main road encircling Vesuvius-Somma on N. and E. — Vertical, $\frac{1}{6}$ the actual scale.

Piazza S.-Francesco
Ottajano

S. Giuseppe di
Ottajano

N. entrance
to Casili

S. entrance
to Casili

S. of.
Terzigno

Vallone
del Purgatorio

Vallone
S. Patrizio

Essential
Scoria

Accessory
lapilli

Dust or
sand

Plate XXI.
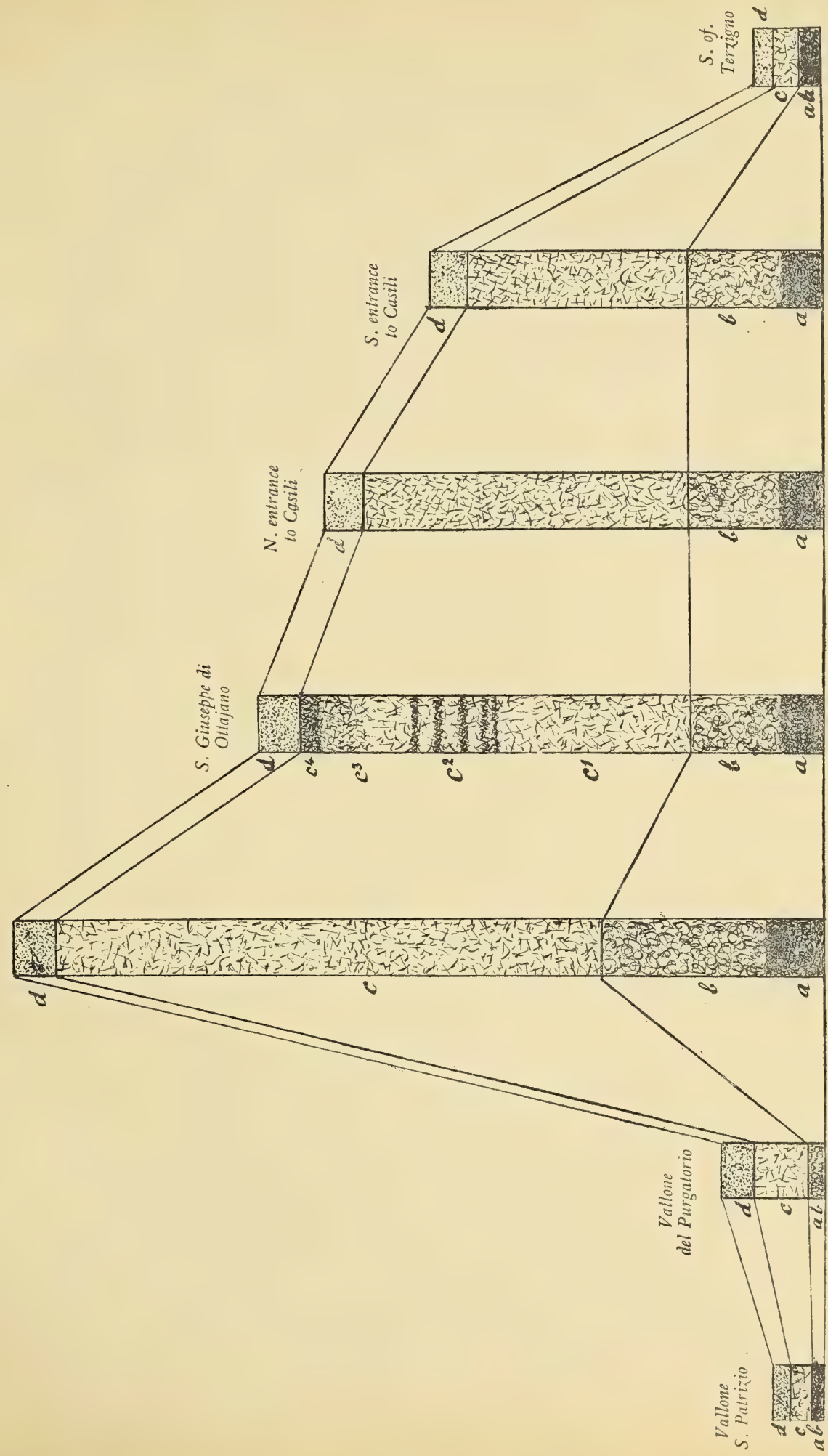
Sections obliquely from N. to W. of Vesuvius-Somma. — Vertical, $\frac{1}{5}$ the actual scale.

Piazza S.-Francesco
Ottajano

d
c
b
a

Punta del Nasone
Summit of Somma

d
c
b
a

Atrio del Cavallo
midway between
base of Cone and Colle
Umberto

d
e^2
e^1
a.b.c

Cancello di Cook
on Salvatore
Ridge

d
e^2
e^1
a.b

Eremo. n.r Observatory
on well sheltered roof

d
e^2
e^1
a.b

Essential
scoria

Accessory
lapilli

dust or
sand

Plate XXII.

Scala di 1 : 25000

Plate XXII.

CONO VESUVIANO

(DOPO L' ERUZIONE DELL' APRILE 1906)

PLATE XXIII.

Longitudine dal meridiano di Roma (Monte Mario)

Scala nel rapporto di 1 a 10.000.

L'equidistanza delle curve è di metri 5

Riproduzione riservata

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Levata nel 1900

Mappatore

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IX.

THE SECONDARY RADIATION EXCITED BY γ RAYS.

BY

F. E. HACKETT, M.A., Ph.D., University College, Dublin.

[COMMUNICATED BY PROFESSOR J. A. McCLELLAND, M.A., D.SC.]

IX.
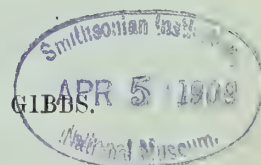
THE SECONDARY RADIATION EXCITED BY γ RAYS.

By F. E. HACKETT, M.A., Ph.D., University College, Dublin.

[COMMUNICATED BY PROFESSOR J. A. McCLELLAND, M.A., D.SC.]

THE research described in this paper deals with an investigation of the manner in which the secondary radiation excited by γ rays varies with the atomic weight of the substance. It has been shown by McClelland[*] that the secondary radiation excited by β rays has a close connexion with the atomic weight of the excited substance, and varies in such a way that, from this electrical standpoint, the elements are arranged into the same periods as those employed by Mendeleef in his chemical classification of them. Since then J. J. Thomson[†] has shown that similar relations exist for the secondary Röntgen radiation; and Barkla has found that the absorbability of this radiation depends on the atomic weight of the substance which emits it.

It is therefore interesting to determine how far such a relation holds for the secondary radiation excited by γ rays; for it may contribute some light on the constitution of matter, and also on the γ rays themselves.

The subject has been touched on in a general manner by Eve and other observers; and more recently papers have been published by Kleeman,[‡] dealing in a detailed manner with the subject, and giving measurements of the intensity of radiation from different elements. His method of measurement and the numbers he obtained differ considerably from those described in the present paper. They will be discussed in the course of the paper. Bragg has also published some results which agree in a general way with the present work, though his theoretical standpoint is different. It may be stated here that the present results can be explained equally well on his theory of the constitution of γ rays, or on the ether-pulse theory.

The results of the present investigation show that the separation of the elements into periods is not so marked as in the other cases already mentioned.

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[*] J. A. McClelland, Trans. Roy. Dub. Soc., vol. ix., 1905.
[†] "Conduction of Electricity through Gases," 2nd ed., p. 395.
[‡] R. D. Kleeman, Phil. Mag., Nov., 1907; May, 1908.

The intensity is practically the same for all elements whose atomic weight lies below 150, but shows a great increase for lead and the other elements which belong to the same period, and a second marked increase for uranium, the element of highest atomic weight which makes up a period with the radio-active elements, radium and thorium.

When γ rays pass through a plate, they may produce an emission of secondary radiations of various kinds; but it is only the penetrating kind, consisting of β rays, or corpuscles travelling with high velocities, which is measured in this paper.

Apparatus.

In these experiments the source of the γ rays was 50 milligrammes of

radium bromide enclosed in a glass vessel, sealed so that no emanation escaped during the observations. The radium (*R*, in figure) was placed at the bottom of a hole in a rectangular block of lead, which was built up of smaller blocks whose dimensions were 9 cm. × 7 cm. × 5 cm. The aperture defining the pencil of γ rays was made by two lower blocks, each with a cylindrical hole in the centre, and a third with a conical opening, so as to obtain a well-defined pencil combined

with effective screening. To ensure complete absorption of the β rays from the radium, the opening was covered with a sheet of lead 2 mm. thick. The system of blocks (*L*) was mounted so that the pencil of γ rays travelled upwards at an angle of 45° to the vertical, and was incident, therefore, at the same angle on the lower surface of a horizontal plate (*P*), which was supported just over the opening. The γ rays passing through the plate produce secondary radiation through its volume, which emerges at both the lower and upper surfaces of the plate. It seemed at first that it was a matter of indifference on which side the radiation was observed. With β and X rays, it is only possible to measure the radiation on the side on which the rays are incident. This method is not applicable here. For, though the β rays from the radium are entirely stopped by the glass and the sheet of lead (*M*) placed over the opening, the pencil of γ rays still contains the secondary β rays which they themselves have produced in passing through the lead sheet. These β rays produce a tertiary radiation on the lower surface of the plate, which vitiates all observations made on this side. In fact, when measurements are made on the side of the plate on which the γ rays are incident, one is really dealing in a large measure with effects produced by β rays.

A method had, therefore, to be devised to enable measurements to be made of the radiation emitted at the upper surface of the plate. Its intensity was measured by the ionisation it produced in a brass cylinder (*A*), whose radius was 5 cm. and length 20 cm. The end nearest the plate (*P*) was covered with a sheet of tinfoil, ·01 mm. thick; while the other end was stopped by a paraffin cork insulating an inner terminal (*B*), which ran along the axis of the cylinder, and was connected to a Dolezalek electrometer. The outside of the cylinder was charged to a positive potential of 240 volts, sufficient to give the saturation current, and the rate of charge of the inner terminal measured in the usual way.

The cylinder and the emerging pencil of γ rays were on the opposite sides of the normal to the plate, which made an angle of 45° with the axes of both in a vertical plane. This angle was selected merely for the sake of symmetry and convenience.

The secondary radiation from the plate passed through at least 12 cm. of air and a sheet of tinfoil before reaching the cylinder, so that, as was mentioned in the beginning of the paper, it is only a penetrating radiation which was observed.

THE METHOD OF OBSERVATION.

The method of observation employed depended on the fact that none of the direct pencil of γ rays coming through the conical opening passed through any part of the cylinder; the latter was brought as near to the plate as was

consistent with this condition, in order to obtain numbers easily observed. To carry out this method, a lead stopper, in shape like the frustrum of a cone, was cast to fit perfectly into and fill completely the conical opening. It was 5 cm. in height, and was found to absorb 95 per cent. of the γ rays which fell on it. This was used to separate out the ionisation produced by the radiation from the plate from the total ionisation in the cylinder. This total ionisation was due to several causes :—(1) the natural ionisation ; (2) the rays which have not passed through the conical opening, but which have reached the cylinder directly through the lead screening, and the secondary effects due to these rays; (3) the secondary radiation produced by the γ rays which pass through the conical opening, and fall on the exposed plate of the substance under examination. The insertion of the lead stopper in the conical opening leaves the first two unchanged, and reduces the third to 5 per cent. of its former value. The difference in the readings before and after the lead stopper is inserted is therefore the secondary radiation produced in the exposed plate by the 95 per cent. of the γ rays absorbed by the stopper.

The essential condition in this method is that the horizontal plate should be large enough to shield the cylinder completely from all parts of the conical opening, so that no secondary rays produced at the edges of the conical opening can reach the cylinder, but are completely absorbed by the plate. If this is so, the difference in the two readings can only be due to the change in the radiation from the plate caused by the absorption of the γ rays producing it. There is no difficulty in getting large plates of the common elements. The general properties of the secondary radiation were therefore investigated with large plates of lead, copper, and aluminium, using a large opening to get a strong pencil of γ rays. But, in making a general comparison of the radiating powers of the elements, a smaller opening, with a lead stopper corresponding, was made in order to make use of a collection of metal plates 5 cm. sq., brought together by Professor McClelland for his researches on β rays. When plates of the elements were not obtainable, powders in trays of the same size were used instead, as no sensible difference between the metal and its powder could be observed in those cases where both were available. It may be added that the plates and layers of powder must be thick enough to absorb completely any β radiation falling on their under-surface, coming from the sides of the opening below.

The secondary radiation excited by the γ rays comes from a small depth below the surface. The intensity of the exciting rays may then be taken as the intensity of the γ rays after they have passed through the plate. If each plate were used singly, the radiation would vary, both from the change in the substance, and in the intensity of the exciting rays. This difficulty is easily avoided by allowing the γ rays to pass through two plates by placing one over

the other. The intensity, then, after transmission is unaltered if the plates are interchanged; and their radiating powers under the same intensity of γ rays is immediately obtained. If the rays were homogeneous, this assumption would not require verification. But, owing to the heterogeneity of the γ rays, it was confirmed by direct experiment that the intensity of the rays after transmission through two or even three of the plates used in these observations was independent of their order of arrangement.

In actual practice it was difficult to obtain numbers with the incomplete apparatus just described. The amount of secondary radiation due to γ rays is small. The numbers for the radiation from lead obtained with this apparatus were of the same order of magnitude as the natural β radiation from a tray of uranium powder of the same size. To obtain numbers it was necessary to join up the inner terminal direct to the quadrant of the electrometer without any additional capacity, and to encase the connexions everywhere in glass tubes filled with paraffin and covered with tinfoil. The wire from the terminal was thus completely shielded and protected from disturbing influences of ionised air. There was no difficulty in obtaining steady readings. Under these conditions the readings for lead were 90 and 60 respectively, giving thirty divisions per minute for the secondary radiation from lead. The correction here is too large to obtain the difference accurately, and there was, from its character, no direct means of further reducing it. An additional capacity reduces both numbers at the same rate, which is no gain. This difficulty was surmounted by the introduction of the compensating device shown in the figure. The wire from the inner terminal ran through a short brass tube (*C*) along its axis, insulated and supported by the paraffin plugs which closed each end of the tube. The length of the tube was 20 cm., and its diameter 6 cm. The outside of the tube could be connected to a high potential of the opposite sign to that of the large cylinder. A small quantity of radium (*S*) brought near the tube produced a current in it to the inner wire, which partially or even completely neutralised the current to the terminal in the large cylinder. By this means the correction was reduced to a convenient magnitude. It was comparatively easy to obtain a null point, such that the spot of light of the electrometer would not move more than one or two divisions in three minutes; but it was found simpler to have a slow rate of deflection for the correction. There is no trouble in arranging this; and the manner of taking the observations remains unchanged.

RESULTS.

The results of the investigation are given in Table I. In this table the elements are separated into their chemical periods. It will be noticed that the first two chemical periods, in so far as they are represented, stand out from the

rest and from each other in their power of emitting secondary radiation. But there is no segregation of the rest of the elements into groups, such as exist for the secondary radiations excited by other means. The numbers for these elements do not greatly vary. It would be impossible to measure accurately the difference between them by comparing them directly with lead. They were therefore compared with an element belonging to the same chemical period. The four standards used were : lead, silver, nickel, and aluminium, whose relative radiating powers were very carefully determined in the manner described. An allusion may be made here to some modifications of this method used to reduce the labour of obtaining the remaining numbers. In many cases it was the differences of the radiating powers of the two elements which were measured and reduced to the standard in the usual way. Or three plates were used, and the known differences of two were used to standardize the unknown difference of a second pair. In this method the position of the radium is indifferent, since a change in the order of arrangement is the only one made. The differences may then be increased by bringing the radium close to the plates.

The absence of any periodic grouping made it unnecessary to include in the list a great number of elements, unless those of high atomic weight. For these the list was made as complete as possible. But no effort was made to ascertain the exact order of arrangement in the case of those elements which have almost equal intensities of secondary radiation.

TABLE I.

Substance.	Secondary Radiation.	Atomic Weight.
Uranium, . .	117	239·5
Uranium Oxide, .	120	—
Bismuth, . . .	100	208·5
Lead, . . .	100	206·9
Mercury, . . .	94	200·3
Platinum, . .	95	194·8
18-ct. Gold, . .	91	—
Tungsten, . .	96	184·0
Tin, . . .	71	118·5
Cadmium, . .	68	112·4
Silver, . . .	69	107·9
Selenium, . .	67	79·1
Zinc, . . .	70	65·4
Copper, . . .	67	63·6
Cobalt, . . .	69	59·0
Nickel, . . .	69	58·7
Iron, . . .	69	55·9
Aluminium, . .	75	27·1

DISCUSSION.

Our ignorance of the exact nature of the γ rays is no bar to a theoretical discussion of the secondary radiation excited by them. Even the recent addition of Bragg's revolving-couple theory to the earlier ether-pulse theory does not introduce any complication if rightly considered. In Bragg's theory the γ rays consist of neutral systems formed by positive and negative particles, revolving about each other, and the whole moving in a direction in the plane of their orbit. The absorption of the γ rays takes place by the collision of the system with an atom and the resultant absorption of the positive particle, while the negative particle passes on, constituting the secondary radiation on emission from the plate.

But for a discussion of the subject it is not necessary to make use of any physical conception of the nature of γ rays. A stream of radiation is passing through each small element of volume, containing atomic systems of electrons. The interaction between the atomic system and the γ radiation, whatever may be its nature, results in the emission of electrons from the element. Each element of volume becomes a source of β rays, the intensity of which depends on the amount of energy absorbed from the γ rays. The energy emitted as β rays from each element of volume should increase, therefore, as the coefficient of absorption of the γ rays increases. For the time being, the plate under the influence of the rays emits β rays as if it were a radio-active substance. A certain thickness of a radio-active substance which depends on its coefficient of absorption for β rays is sufficient to give the maximum effect. The secondary radiation here also comes from a certain depth below the surface—certainly not from a greater depth than ·05 cm. of tin, the thickness of forty sheets of tinfoil. The intensity of the γ rays does not vary more than 1 per cent. in passing through such a layer, so that the secondary radiation may be considered as coming from a number of sources whose intensity per unit volume is constant. The intensity of the radiation emitted depends on two factors—(1) the intensity of the sources per unit volume, (2) the thickness of the effective layer. The first factor increases with the coefficient of absorption of γ rays. The second factor diminishes evidently with the coefficient of absorption of β rays. Since both coefficients are roughly proportional to the density, they are roughly proportional to each other, so that the change in the intensity due to the first factor might be expected to compensate roughly for the change due to the second factor, which is in the opposite direction. An argument much the same as the above has been used by Bragg to show that the two factors work against each other, and may be expected to balance each other, as they actually do.

These general considerations explain why DENSITY has little effect in

determining the radiation from different substances. The more complete discussion, later in the paper, affords an explanation of the actual differences between the amounts of radiation from the various elements.

If these physical ideas are translated into mathematical language, the same result is obtained, but in a more precise form. The treatment already given by McClelland in his papers on secondary radiation due to β rays is easily adapted to the case of γ rays. He assumed that a certain fraction κ of the energy of the β rays absorbed in each element of volume is re-emitted as secondary β rays. As a first approximation, half of the secondary rays may be taken as travelling in the same direction, and half in the opposite direction. This has been found sufficient in discussing all the experimental facts. It will be noticed that this manner of looking at this type of secondary radiation of β particles covers equally well all the hypotheses—(1) that they are scattered β particles of the primary stream, then κ is the coefficient of scattering; (2) that they are electrons expelled from the atom; (3) that they consist of a mixture of both.

In the case of γ rays, we can assume, according to Bragg, that the emission of secondary radiation of β particles takes place in the same direction as the exciting radiation; but this is not a special consequence of Bragg's theory; it is equally possible on an ether-pulse theory. Such an effect might possibly exist in the case of β rays; but it would be obscured by the effect of scattering of the rays, which makes it difficult to distinguish even the true secondary radiations, as a whole, from the total scattering.

On the other hand, the same approximation as for β rays may be adopted, that half of the secondary goes initially in the same direction as the primary, and half in the opposite direction. This has been done for symmetry below. It is easy afterwards to deduce the result of assuming that it all goes initially in one direction.

Let the energy of γ rays incident normally per unit area on a plate AB be denoted by R_0, and the energy passing down through unit area of a depth x be R. If μ_γ be the coefficient of absorption of γ rays, the amount of energy absorbed in the layer dx is $\mu_\gamma R dx$. The amount of secondary radiation generated in the layer will be $\kappa_\gamma \mu_\gamma R dx$, if we assume that the energy of the emitted secondary rays bears a constant ratio (κ_γ) to the energy absorbed. Let the downward flow of secondary radiation be S, and the upward flow s. This secondary radiation of β rays excites a tertiary radiation in each element of volume through which it passes. If μ_β be the true coefficient of absorption of β rays, this effect at a depth x is represented by two terms, each similar to that for γ rays $\mu_\beta \kappa_\beta [S + s]$. The total energy set free as secondary radiation in the layer dx per unit area is $(\mu_\gamma \kappa_\gamma R + \mu_\beta \kappa_\beta [S + s]) dx$. According to what has been said above, half may be taken as travelling upwards, and half downwards.

With this notation we have the following equations :—

$$\frac{dR}{dx} = -\mu_\gamma R.$$

$$\frac{dS}{dx} = -\mu_\beta S + \tfrac{1}{2}\left[\mu_\gamma \kappa_\gamma R + \mu_\beta \kappa_\beta (S + s)\right],$$

$$-\frac{ds}{dx} = -\mu_\beta s + \tfrac{1}{2}\left[\mu_\gamma \kappa_\gamma R + \mu_\beta \kappa_\beta (S + s)\right];$$

or

$$R = R_0 e^{-\mu_\gamma x}$$

$$\frac{dS}{dx} = -aS + bs + cR\,; \quad -\frac{ds}{dx} = -as + bS + cR.$$

A solution of these equations is given by

$$S = Ae^{-\lambda_\beta x} + Be^{+\lambda_\beta x} + cLR_0 e^{-\mu_\gamma x},$$

where

$$\lambda_\beta = \mu_\beta \sqrt{1 - \kappa_\beta},$$

$$L = \frac{\mu_\beta + \mu_\gamma}{\lambda^2_\beta - \mu^2_\gamma}.$$

The constants A and B have yet to be determined by the conditions $S = 0$ when $x = 0$; $s = 0$ when $x = d$ where $d =$ thickness of plate. The expressions obtained are complicated for the general case, but assume a simple form for the particular case to which the observations apply. McClelland[*] has shown that λ_β is the apparent coefficient of absorption of β rays, so that if plates thick enough to absorb β rays falling on the upper side are used, $e^{-\lambda_\beta d} = 0$, and also μ_γ/λ_β may be neglected in comparison with the other terms.

We find

$$A = -cLR_0, \quad Ae^{-\lambda_\beta d} = 0,$$

$$B = 0, \qquad Be^{+\lambda_\beta d} = -\frac{c[L(a - \mu_\gamma) - 1]}{a + \lambda_\beta} R_0 e^{-\mu_\gamma d}.$$

Inserting these values, we obtain for S_d, the secondary radiation emerging on the same side of the plate as the γ rays,

$$S_d = R_0 e^{-\mu_\gamma d} \frac{\mu_\gamma \kappa_\gamma}{\lambda_\beta (1 + \sqrt{1 - \kappa_\beta})}. \qquad [A]$$

The term $R_0 e^{-\mu_\gamma d} \mu_\gamma \kappa_\gamma$ is the amount of secondary radiation excited per unit volume in the surface layer.

[*] J. A. McClelland, Trans. Roy. Dub. Soc., vol. ix., part iv., 1907.

2 L

The value of S is identical with the value which would be obtained for a radio-active substance emitting only β rays, whose intensity of radiation was $R_0 e^{-\mu_\gamma d}\mu_\gamma \kappa_\gamma$ per unit volume, when secondary effects are considered. The approximation $\mu_\gamma/\lambda_\beta = 0$ is equivalent to considering the intensity of the rays constant in the layer from which the β rays come, and writing $e^{-\lambda_\beta d} = 0$, to considering only a small thickness on one side of the plate important.

The expression for the secondary radiation emerging from that side of the plate on which the rays are incident will be obtained from the above by the omission of $e^{-\mu_\gamma d}$. It is clear that it should be the same fraction of the intensity of the primary passing through the surface layer in both cases.

$$s_0 = R_0 \frac{\mu_\gamma \kappa_\gamma}{\lambda_\beta (1 + \sqrt{1 - \kappa_\beta})}. \qquad [B]$$

If we assume that all the secondary radiation excited by γ rays goes initially in the direction of the primary rays, then we have the equations :—

$$\frac{dR}{dx} = -\mu_\gamma R,$$

$$\frac{dS}{dx} = -\mu_\beta S + \tfrac{1}{2}\mu_\beta \kappa_\beta [S + s] + \mu_\gamma \kappa_\gamma R,$$

$$-\frac{ds}{dx} = -\mu_\beta s + \tfrac{1}{2}\mu_\beta \kappa_\beta [S + s] ;$$

or

$$R_0 = R_0 e^{-\mu_\gamma x},$$

$$\frac{dS}{dx} = -aS + bs + 2cR,$$

$$-\frac{ds}{dx} = -as + bS.$$

A solution of these equations is given by

$$S = A e^{-\lambda_\beta x} + B e^{+\lambda_\beta x} + 2cMR_0 e^{-\mu_\gamma x}.$$

$$bs = (a - \lambda_\beta)A e^{-\lambda_\beta x} + (a + \lambda_\beta)B e^{+\lambda_\beta x} + 2cR_0 e^{-\mu_\gamma x}[M(a - \mu_\gamma) - 1],$$

where

$$\lambda_\beta = \mu_\beta \sqrt{1 - \kappa_\beta},$$

$$M = \frac{a + \mu_\gamma}{\lambda_\beta^2 - \mu_\gamma^2}.$$

Proceeding exactly as before, we obtain for S_d and s_0 the expressions

$$S_d = R_0 e^{-\mu_\gamma d} \frac{\mu_\gamma \kappa_\gamma}{\lambda_\beta}. \qquad [C]$$

$$s_0 = R_0 \frac{\mu_\gamma \kappa_\gamma}{\lambda_\beta}\ \frac{1 - \dfrac{\kappa}{2} - \sqrt{1 - \kappa}}{\dfrac{\kappa}{2}} = R_0 \frac{\mu_\gamma \kappa_\gamma}{\lambda_\beta} p, \qquad [D]$$

where $p*$ is the fraction of a primary beam of β rays, falling normally on a plate thick enough to absorb it, which is returned as secondary. It has been determined experimentally by McClelland, in the case of lead, to be 49 per cent.; for other substances it diminishes with atomic weight, having a value of about 24 per cent. for aluminium.

It would be important to obtain measurements of the secondary radiation produced by a pure pencil of γ rays on the side of the plate on which the rays are incident, using a magnetic field to remove the β rays which always accompany the γ rays when such a precaution is not taken. It would not be necessary to make such measurements with great accuracy, for there is sufficient range in the value of p for different substances to enable us to decide if the relation indicated by formulas (C) and (D) holds good, and thus to discover to what extent the γ rays have any directive action on the β rays produced by them.

For the discussion of the experimental results in this paper, we use the expression (A) or (C) for S_d, the secondary radiation emerging from the plate on the same side as the γ rays. It does not matter which formula is used, since the expressions in each case for the radiation emerging from the plate on the same side as the primary are very much alike and can be discussed together. The only difference is the factor $1 + \sqrt{1 - \kappa_\beta}$ in the denominator of one. From Table II. it will be seen that it does not vary much from one element to another.

The values of λ_β and κ_β have as yet only been determined for the β rays of radium and the secondary radiation produced by them. From some experiments at the end of this paper, it is seen that the penetrating power of the secondary rays produced by γ rays is somewhat less than the penetrating power of the β rays from uranium. The ratios of the two coefficients of absorption for tinfoil in the case of the secondary rays from aluminium is 1·83, and from lead varies from 2·34 to 1·41. As the uranium β rays are not so penetrating as the β rays from radium, it is likely that κ_β is less for these secondary β rays than for the β rays of radium; but it probably varies in the same way with the atomic weight. As before, since the absorption coefficients of γ rays and β rays in general are each roughly proportional to the density, their ratio is nearly constant from one element to another, and contributes nothing to the variation in the secondary radiation from one element to another. A glance at the values of $1 + \sqrt{1 - \kappa_\beta}$ given in Table II. will show that it decreases slowly with increase of atomic weight. In this case also it may be assumed that it varies in a similar manner. We therefore conclude from both (A) and (C) that the great increase in the secondary radiation for elements of high atomic weight is because κ_γ is very much greater for these elements. This coefficient has considerable

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* J. A. McClelland, " Energy of Secondary Radiation."—Trans. Roy. Dub. Soc. vol. ix., part ii., 1906.

interest; but the particular physical expression we give to it depends on the view taken of the mechanism of the absorption of β rays, and the emission of secondary radiation. If we assume the γ rays are ether-pulses, it is highly improbable that the β particles emitted acquire their velocities under the influence of the electric forces in the γ rays. The energy of the γ rays absorbed by the atom must be regarded as acting like a detonator. It upsets the stability of the atomic grouping, causing the expulsion of one or more β particles, carrying a part of the atomic energy with them. Since μ_γ is the fraction of the incident energy absorbed per unit volume, and $\mu_\gamma \kappa_\gamma$ the amount of energy emitted as β rays, κ_γ is an index of the explosiveness of the atom in producing an expulsion of electrons by the absorption of a given amount of the energy from the incident γ rays. From the reasoning given above, it would seem as if κ_γ were constant for elements of moderate atomic weight, but had a marked increase for such elements as platinum, lead, and uranium.

The Secondary Radiation per Atom.

The expressions deduced for s_d can be discussed from another standpoint which is of interest. The term $R_0 e^{-\mu_\gamma d} \mu_\gamma \kappa_\gamma$ is the amount of secondary radiation excited per unit volume in the surface layer. If we write $R_0 e^{-\mu_\gamma d} \dfrac{\mu_\gamma \kappa_\gamma M}{\rho} = \sigma$ where M is the atomic weight and ρ is the density, then σ is proportional to the secondary radiation per atom when a substance is traversed by γ rays. We have then

$$S_d = \frac{R_0 e^{-\mu_\gamma d} \mu_\gamma \kappa_\gamma}{\lambda_\beta (1 + \sqrt{1 - \kappa_\beta})} = \frac{R_0 e^{-\mu_\gamma d} \mu_\gamma \kappa_\gamma \; M/\rho}{M/\rho \; \lambda_\beta (1 + \sqrt{1 - \kappa_\beta})} = \frac{\sigma/M}{(1 + \sqrt{1 - \kappa_\beta})\lambda_\beta/\rho} \tag{A}$$

$$S_d = \frac{R_0 e^{-\mu_\gamma d} \mu_\gamma \kappa_\gamma}{\lambda_\beta} = \frac{\sigma/M}{\lambda_\beta/\rho} \tag{C}$$

It has already been stated that we know λ_β and κ_β only for the β rays of radium. But if we use the values given by McClelland, we find that $\lambda_\beta/\rho \, (1 + \sqrt{1 - \kappa_\beta})$ is almost constant (Table II.), and the change in λ_β/ρ is not great compared with the change in atomic weight.

If these results hold true, as they most probably do, for the β rays in the secondary radiation we are discussing, it follows that the denominator $[(1 + \sqrt{1 - \kappa_\beta})\lambda_\beta/\rho$ or $\lambda_\beta/\rho]$ in formula (A) or (C) must be nearly constant; and whichever formula we adopt, we conclude that σ/M is approximately proportional to S_d, the secondary radiation.

Table II.

Element	λ	$\sqrt{1-\kappa}$	ρ	$\lambda\beta/\rho$	$\lambda\beta/\rho(1+\sqrt{1-\kappa\beta})$
Lead, .	91	·339	11·4	8·0	10·7
Platinum, .	175	·339	21·5	8·0	10·9
Tin, .	54	·406	7·3	7·4	10·4
Cadmium, .	66	·412	8·6	7·5	10·6
Silver, .	85	·418	10·5	8·0	10·3
Zinc, .	48	·464	7·2	6 6	9·6
Copper, .	50	·469	8·9	5·6	8·3
Nickel, .	63	·495	8·5	7·6	11·3
Aluminium,	14	·612	2·7	5·0	8·2

But the relative secondary radiation is practically unchanged as we ascend the elements in the table of atomic weights from aluminium to tin, so that σ/M must be almost constant for atomic weights ranging from 27 to 120, but increases very rapidly for lead and platinum. These results may therefore be summed up in the broad general statement that the secondary radiation per atom (σ) excited by γ rays is roughly proportional to the atomic weight when this does not exceed 120, but increases more rapidly than the atomic weight for elements like lead, platinum, and uranium. J. J. Thomson has advanced the hypothesis that the number of electrons in the atom is equal to or of the same order as the atomic weight. The above result accords with this view if we suppose that, for the smaller atomic weights, the chance of the expulsion of an electron from an atom, whose stability is disturbed by a penetrating type of rays such as γ rays, is independent of the atomic grouping, and proportional simply to the number of electrons in the atom.

If the substance were in the form of a gas, then the ionisation in the gas would be due in part to this penetrating secondary radiation (σ), and to the ionisation produced by β particles so expelled from the atom, and in part to any other type of secondary radiation (σ') which may exist, but which is easily absorbed, and so is not measured in the foregoing method. The second part will be in a constant ratio to the first, if the ionising power of the secondary β rays does not vary for different substances. The results at the end of this paper show that they have the same order of penetrating power, and so can be assumed to have the same ionising power. In this case, the ionisation per unit volume would be proportional to $\sigma (1 + C) + \sigma'$ where C is a constant. Kleeman* has determined the ionisation produced in gases by γ rays, and has found it to be an additive quantity for the atoms in the molecule. He has thus been able to deduce the relative ionisation per atom. His numbers are given below.

* R. D. Kleeman, Proc. Roy. Soc., A vol. lxxix., p. 220, 1907.

TABLE III.

Element.	Relative Ionisation per atom.	Atomic weight.	Relative Ionisation.
			Atomic weight.
Hydrogen, . .	0·18	1·008	·180
Carbon, . .	0·46	12·00	·038
Nitrogen, . .	0·45	14·04	·032
Oxygen, . .	0·58	16·00	·036
Sulphur, . .	1·60	32·06	·050
Chlorine, . .	1·44	35·45	·046
Bromine, . .	2·81	79·96	·035
Iodine, . .	4·50	126·85	·035

From the numbers in the fourth column of Table III. it will be seen that the ratio of the relative ionisation per atom to the atomic weight tends towards a constant value for a change of atomic weight from 12 to 126. It was deduced that the relative ionisation is proportional to $\sigma (1 + C) + \sigma'$; and direct measurements on the penetrating secondary radiation have shown that σ increases at the same rate as the atomic weight. Both lines of work will be in complete accord if we make either of the probable assumptions that the easily absorbed secondary radiation is either small in proportion to σ, or bears a constant ratio to it.

KLEEMAN'S OBSERVATIONS.

Kleeman[*] has recently determined the secondary radiations from different substances by another method. He allows the γ rays, after passing through a sheet of lead and the side of an aluminium box, to fall directly on the plate, and measures the secondary radiation produced. In such a method the exciting radiation consists not only of the γ rays, but also of the β rays produced by them in passing through the aluminium. If the latter were unimportant, the method would be accurate. But this is not so, as the author found in some preliminary experiments which led him to adopt the method described in this paper. The numbers given by Kleeman differ widely from those given in Table I.; instead of the secondary radiation remaining nearly constant for a wide range of atomic weight, he finds it increases with the atomic weight in the same manner as it does for β rays or X rays, which would be the result obtained if in the exciting radiation there were a large amount of β rays.

Bragg offers another explanation of Kleeman's results from the point of view of his theory of the γ rays. On this theory the secondary radiation from the face of a plate on which the rays are incident should be less than from the other

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[*] R. D. Kleeman, Phil. Mag., Nov., 1907.

face, as the β particles are initially projected in the direction of the γ rays. Further, as is shown by the equations (*C* and *D*), the radiation from the incident face is approximately the fraction *p* of that from the emergence face, where *p* is the ratio of secondary to primary radiation when the primary consists also of β particles. Since, therefore, the secondary radiation from the emergence face when γ rays are used is constant, at least for substances of low atomic weight, the radiation from the incident face should vary in the same general way as for β rays. Such is the natural interpretation of Kleeman's results on Bragg's theory of the γ rays. But, as pointed out earlier in this paper, further measurements are required of the secondary radiation from the incident face, care being taken to use a primary beam of rays free from β particles. And further it is clear that equations similar to *C* and *D* will hold on any theory of the γ rays, the ether-pulse theory included, which admits the possibility of the β particles being projected initially in the direction of the γ rays.

THE PENETRATING POWER OF THE SECONDARY RADIATION.

The apparatus used in making the above observations also served for making an examination of the penetrating power of the secondary rays. A measurement of the secondary radiation was made in the manner described with one sheet of tinfoil, covering the end of the ionisation cylinder and a second measurement with five sheets of tinfoil as a covering. The ratio of these two measurements (ρ) gives an approximate value for the relative penetrating powers of the rays from different substances. To standardize these observations the radium was removed, and a similar observation was made on the penetrating power of the rays from a tray of uranium oxide of exactly the same size placed in the same place as the plates used. The penetrating power of secondary radiation from uranium oxide itself was also determined in the same way as for the other substances. The ratio for the natural radiation from uranium oxide was found to be ·77. If we take its coefficient of absorption as 100, we can obtain the relative coefficients of absorption [λ_β', λ_β'', λ_β'''] for the secondary rays excited by γ rays of different penetrating powers. These are easily obtained by placing over the conical hole lead plates and blocks of lead cast to fit the opening.

An auxiliary series of observations, using the same arrangement of screening with the γ rays falling directly on an ionisation cylinder closed with a sheet of lead 2 mm. thick, gave an approximate measure of the intensity of the γ rays.

The coefficient of absorption of the rays after transmission through the lead screens was measured by placing a thick sheet of metal in front of the cylinder, and then interposing a second sheet of the same thickness in the path of the rays.

The values given under $[\lambda_\beta', \lambda_\beta'', \lambda_\beta''']$ have been measured very carefully in this way. The results of these observations for lead, copper, and aluminium, which were taken as typical substances, are exhibited in the following table :—

TABLE IV.

Substance.	ρ'	λ_β'	λ_γ'	ρ''	λ_β''	λ_γ''	ρ'''	λ_β'''	λ_γ'''
Uranium oxide,	·44	313							
Lead, . .	·54	234	1·090	·60·	194	—	·69	141	·660
Copper, . .	·59	200	0·765	·63	176	—	·64	168	·370
Aluminium, .	·62	183	0·184	·62	183	·141	·62	183	·122
Intensity of γ rays,	100			83			50		
Thickness of lead sereen,	—			2 mm. lead			10 mm. lead		

For the β rays from uranium oxide, $\rho = ·77$; $\lambda_\beta = 100$.

The observations fall into three groups depending on the type of γ rays used to excite the secondary rays. In all the experiments the radium was contained in a sealed glass tube, which absorbed nearly all the β rays, and of course some of the very easily absorbed γ rays. In the first series the γ rays were incident directly on the under-surface of the plate, thick enough to absorb all the β rays (2 mm. for lead, 6 mm. for aluminium). The secondary radiation from the upper surface is therefore excited by an easily absorbed type of γ rays. In the other two series the γ rays traversed the lead screens before falling on the plate.

Before discussing these results, it should be pointed out that the method of measurement is only approximate. It would be an accurate method if the lead frustrum 5 cm. thick absorbed all the γ rays; but, as was remarked earlier, it only absorbs 95 per cent. The error involved is small. Let

S = intensity of secondary rays excited by γ rays ;

F = fraction transmitted through four additional sheets of tinfoil ;

$s \,\&\, f=$ similar magnitudes for the secondary rays excited by the rays after passing through the lead frustrum.

$$\rho = \frac{FS - fs}{S - s} = \frac{F\left[1 - \dfrac{fs}{FS}\right]}{\left[1 - \dfrac{s}{S}\right]}$$

These observations, therefore, only give F when there is no variation in the penetrating power of the secondary rays. Where such a variation exists, the

method magnifies it slightly. On the above scale of intensity $s = 5$; and if we assume for lead $f = \cdot 77$, an extreme value, the difference made in taking $F = \rho$ is not 2 per cent., so that the method gives fairly approximate values for the absorption-coefficient.

It has been shown theoretically that the absorption-coefficient of the β particle varies inversely as the fourth power of the velocity; and this result is borne out by direct experiment on β rays of different velocities. In the case of secondary rays we have probably a heterogeneous bundle of rays consisting of β particles travelling with different velocities, so that the absorption-coefficient can only indicate the average value of these velocities. Using this result, we can interpret Table IV. as showing that, with increasing hardness of the γ rays, as increased penetrating power may conveniently be termed, the average velocity of the secondary rays increases markedly for elements of high atomic weight such as lead, not so much for elements of medium atomic weight such as copper, and does not vary at all for elements of low atomic weight such as aluminium. For very soft γ rays, it decreases with increase of atomic weight; but for the penetrating γ rays, it increases with the increase of atomic weight.

Innes* has measured directly the velocity of the kathode particles emitted under the influence of Röntgen rays for elements of high atomic weight, such as lead, gold, and silver. He found that the velocity of the fastest increased with increasing hardness of the rays, and that the minimum velocity was nearly the same for all substances. His values for lead ranged from $6\cdot3$ to $7\cdot3 \times 10^9$ cm. per sec. for soft rays, and from $6\cdot3$ to $8\cdot3 \times 10^9$ cm. per sec. for hard rays.

We cannot draw any conclusions concerning the minimum velocity from observations on the absorption-coefficients; but it is clear that both in the case of Röntgen and γ rays, the hardest rays cause the emission of the particles with the highest velocities. This is another similarity between the two types of rays. It is true, of course, that rays might become more penetrating by a proportionate increase in the number of the particles with high velocities. But even on this view, the hard rays cause the greatest emission of the fastest particles.

The comparison between the secondary radiations excited by γ and X rays cannot be carried very far, since, in the former case, the soft type of rays is certainly heterogeneous, and the hard rays have only been obtained by transmission through lead screens. It is not certain whether the hardening of the rays in this way is due to the absorption of the softer rays, or a transformation of the rays by passing through the substance. A more extended series of observations, using screens of different substances, is necessary before we make any wider generalizations or discuss the rival theories in the light of these results.

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* P. D. Innes, Proc. Roy. Soc., 1907.

It will be merely remarked that Bragg's theory, in its present simple form, demands that the secondary β particles from all substances should have the same velocity, and so the same penetrating power, since they are only the negative particles of the revolving couple which constitute the γ rays, moving on alone after the collision with their original velocity. This does not at all agree with the above measurements. As the author is at present engaged in pursuing this investigation, the further discussion of the subject is postponed until a later paper.

SUMMARY.

1. An account of the direct measurement of the secondary radiation emitted from the upper surface of a plate, when γ rays are incident on the lower surface, is given. The pencil of γ rays passes up through the plate at an angle of 45° to the normal. The intensity of the radiation emitted in the plane of incidence in a direction normal to the γ rays is measured by means of an ionisation cylinder.

2. The secondary radiation *thus measured* is nearly constant for all atomic weights ranging from 27 to 120, but increases for the gold-lead-bismuth group of elements, and there is a further increase for uranium.

3. A discussion of these results leads to the conclusion that the secondary radiation per atom is roughly proportional to the atomic weight when this does not exceed 120, and increases more rapidly than the atomic weight for elements of high atomic weight such as lead and platinum.

4. It is shown that this result is in general agreement with the work of Kleeman on the relative ionisation of gases per atom by γ rays, which also increases at the same rate as the atomic weight.

5. The penetrating power of the secondary β radiation diminishes with the increase of atomic weight for soft γ rays, but increases with the atomic weight for hard γ rays.

6. For elements of low atomic weight, as aluminium, the penetrating power of the secondary β radiation does not alter with the penetrating power of the primary ; but it increases with the latter for elements of high atomic weight.

7. The results of this paper do not afford any decisive test between the ether-pulse theory and Bragg's theory.

INDEX TO VOLUME IX.

END OF VOLUME IX.

TRANSACTIONS (SERIES II.).

VOLUME IX.

[This Volume is concluded with the nine Parts here enumerated.]